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ANNUAL CATALYST RESEARCH PROGRAM REPORT. APPENDICES. VOLUME VII

Health Effects Research Laboratory
Research Triangle Park, North Carolina

September 1975

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16. ABSTRACT

This report constitutes the first Annual Report of the ORD Catalyst Research Program required by the Administrator as noted in his testimony before the Senate PUblic Works Committee on November 6, 1973. It includes all research aspects of this broad multi-disciplinary program including: emissions characterization, measurement method development, monitoring, fuels analysis, toxicology, biology, epidemiology, human studies and unregulated emissions control options. Principal focus is upon catalyst-generated sulfuric acid and noble metal particulate emissions.

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UNITED STATES · ENVIRONMENTAL PROTECTION AGENCY

Health Effects Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

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ANNUAL CATALYST RESEARCH PROGRAM REPORT APPENDICES

Volume VII

by

Criteria and Special Studies Office
Health Effects Research Laboratory
Research Triangle Park, North Carolina 27711

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
HEALTH EFFECTS RESEARCH LABORATORY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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ENVIRONMENTAL TOXICOLOGY RESEARCH LABORATORY
NATIONAL ENVIRONMENTAL RESEARCH CENTER
CINCINNATI, OHIO

STUDIES ON CATALYTIC COMPONENTS AND EXHAUST EMISSIONS

Issued August, 1974
by
The Staff of the ETRL

J. F. Stara, Director

INTRODUCTION

Wellington Moore, Jr.

In July, 1973, the Division of Health Effects instructed the ETRL to reprogram ROAP 21 AFK with major emphasis on the toxicologic assessment of catalytic attrition products and automotive emissions which had passed through the oxidization catalyst. Interest in the biological effects of the noble metals (platinum [Pt] and palladium [Pd]) resulted from the decision by the automotive manufacturers to use these metals in the catalytic converter. These converters are designed to reduce the concentrations of carbon monoxide (CO) and hydrocarbons (HC) in the exhaust stream by oxidizing them into carbon dioxide and water. The control of the concentrations of CO and HC in automotive emissions is necessary in order for light-duty vehicles to comply with the CO and HC emission standards set forth in the Clean Air Amendments of 1970. With the use of Pd and Pt in automotive catalytic converters, there is the possibility that some of the material will be emitted to the atmosphere or enter into other segments of the environment following degradation or disposal of worn-out converters.

At the present time, the author is not aware of any information concerning the chemical form of Pd or Pt which may be emitted in the exhaust. It can be speculated that the attrition products from the catalyst could include: 1) particulate composed of the metals combined with substrate material; 2) different chemical forms of Pd and Pt. A survey of the literature indicated that there was very little information on the toxicology of chemical forms of Pt or Pd which might be expected to occur following use of these metals in the catalyst. Likewise, there was no information on the inhalation exposure of animals to exhaust from automobiles containing a catalyst in the exhaust train.

The ETRL research effort was divided into two major segments: 1) toxicological studies on catalytic metals associated with the oxidation catalyst; 2) assessment of the biological effects of automotive emissions which have passed through the oxidative catalytic converter.

In the noble metal studies, the soluble forms of Pd and Pt have been used in order to ascertain some of the basic toxicological and metabolic aspects. It is realized that the availability and metabolism of other chemical forms or substrate material containing Pd or Pt may be different.

It should be emphasized that ETRL has been studying the biological effects of the noble metals for less than a year and the data should be considered as preliminary in nature. The impact of any metal upon a biological system is complex; however, these findings should serve as a basis for additional research in defining the impact of the use of these metals upon the environment. This report presents data on the ETRL studies. A number of these studies have been submitted for publication in the open literature.

TOXICOLOGICAL STUDIES OF PALLADIUM AND PLATINUM

BIOLOGICAL FATE OF ^{103}Pd IN RATS FOLLOWING DIFFERENT ROUTES OF EXPOSURE

W. Moore, Jr., D. Hysell, W. Crocker and J. Stara

It is possible that Pd used in the catalytic converter may appear in the environment if attrition or degradation of the catalytic bed occurs. The major routes of exposure to humans would be through inhalation and ingestion. The purpose of this study was to determine the influence of different routes of exposure upon absorption, tissue distribution and excretion. Placental transfer was determined following intravenous administration.

METHODS

Animals and Treatments

The outbred albino rats (Charles River CD-1 strain) used in this study were maintained on a commercial diet (Purina Lab Chow) and tap water *ad libitum* except where otherwise noted. The three treatment groups consisted of:

1. Intratracheal administration

Ten fasted male rats, 180-200 g, were anesthetized with pentobarbital sodium and placed in dorsal recumbency. The trachea was isolated through a ventral midline cervical incision and blunt dissection of the overlying masculature. $^{103}PdCl_2$ (25 μCi in 0.1 ml saline) was injected intratracheally with a 1 cc tuberculin syringe and 5/8 in., 25 ga needle. After the incision was closed, the animals were maintained in hanging wire cages for 104 days to determine whole body retention of the $^{103}PdCl_2$.

2. Oral administration

Twenty fasted male rats, 180-200 g, were lightly anesthetized with ether and given 25 μCi of $^{103}PdCl_2$ in 0.2 ml saline by stomach tube. Ten rats were placed in metabolism cages for collection of 24 hr. urine and fecal samples to determine routes of excretion. The other ten rats were sacrificed 24 hr. after dosage to establish organ distribution of the $PdCl_2$.

Fifteen nonfasted suckling rats, 30 g were given a single dose of $^{103}PdCl_2$ (25 μCi in 0.2 ml saline) by stomach tube. These animals were maintained to compare their retention of Pd with that of the adult rats.

3. Intravenous administration

Twenty male rats, 180-200 g, were given 25 μCi $PdCl_2$ in 0.1 ml saline intravenously (iv) in a tail vein with a 1 cc tuberculin syringe and 5/8 in., 25 ga. needle. Ten were sacrificed 24 hr. later for organ distribution; ten rats were placed in metabolism cages for collection of 24 hr. samples of urine and feces and subsequent determination of whole body retention. Thirteen female rats (16 days pregnant) were given 25 μCi $^{103}PdCl$ iv and maintained in metabolism cages for collection of feces and urine. They were sacrificed 24 hr. after dosage to determine organ distribution and placental transfer of the $^{103}PdCl_2$. An additional group of 8 female rats were given 25 μCi $^{103}PdCl_2$ iv within 24 hr. post-parturition. The mothers and litters were maintained 25 days to determine if the ^{103}Pd was transferred to the young via the mother's milk.

Sacrifice and Tissue Sampling

All rats were euthanatized with an overdose of chloroform anesthesia. Samples collected routinely were blood, heart, lung, liver, kidney, adrenal, pancreas, abdominal fat, spleen, skeletal muscle, bone, brain, and testicle from males, ovary from females. In the pregnant females, 4 placentas, 4 fetuses, and a pooled sample of fetal livers were also saved. In the young rats from the milk transfer study, lung, liver, kidney, bone, and spleen were saved. Tissue samples were placed in preweighed glass vials for counting.

Radioactive Determinations

$^{103}PdCl_2$, which has a half-life of 17 days, was used in all the studies. Immediately after dosing, whole body gamma counts were made on all animals used in the retention studies. The animals were counted daily for the first few days and then every other day for the duration of the experiment. A 200-channel gamma spectrometer with a 5 in. NaI (Tl) crystal was used for whole body counts. Tissue, urine, and feces samples were counted in a well-type refrigerated scintillation spectrometer.

Whole Body Retention

Analysis of the data for whole body retention of ^{103}Pd following a single exposure disclosed that the route of administration of the dose significantly affected whole body retention. The percent of ^{103}Pd retained with time in the rat following three different routes of administration is presented in Figure 1. Following oral dosing, the retention curve declined very rapidly during the first 3 days to about 0.4% of the initial dose. The initial rapid clearance is attributed to passage of the non-absorbed ^{103}Pd through the gastrointestinal tract. Extrapolation of the

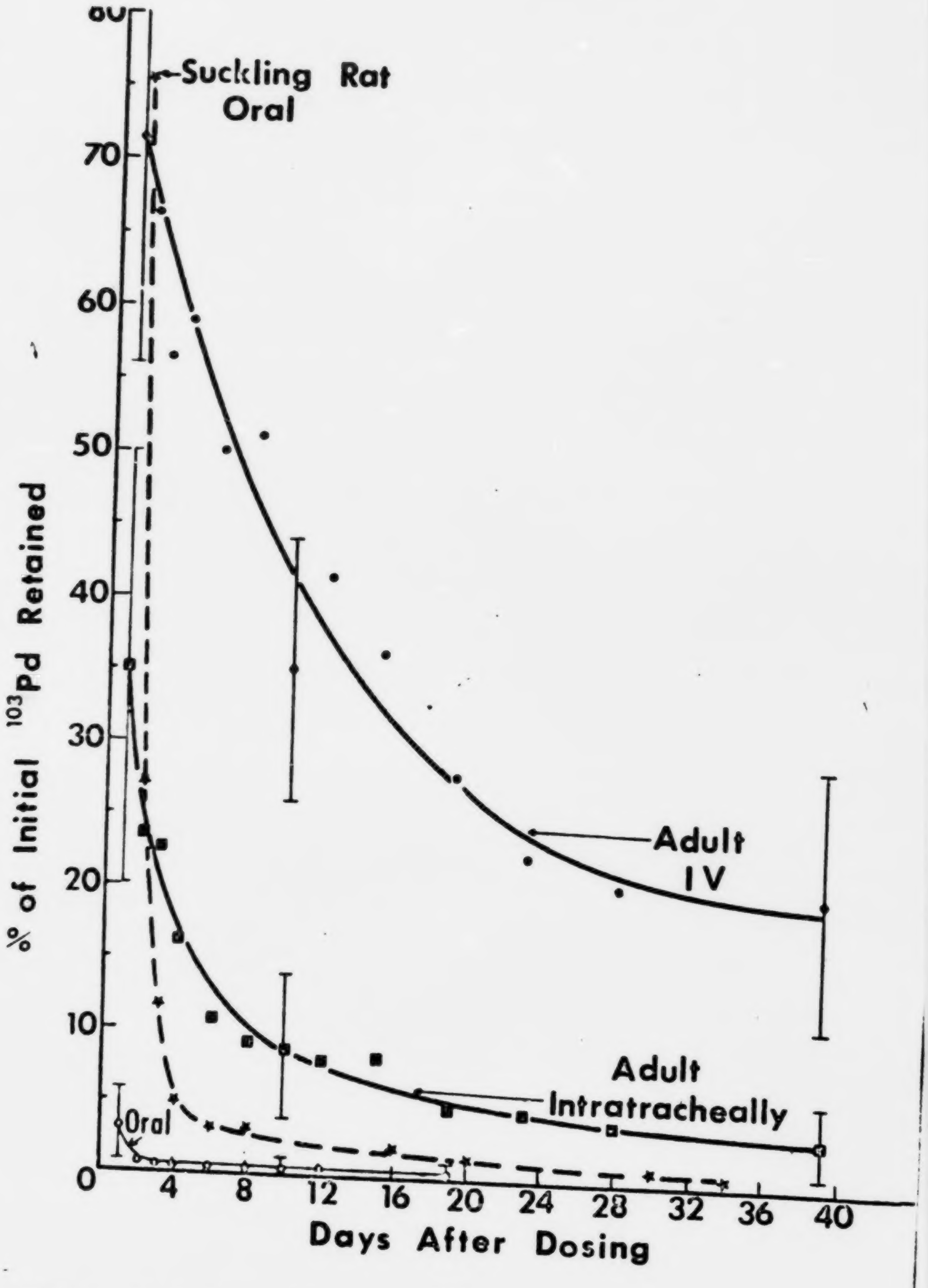

Fig. 1. Whole body retention of ^{103}Pd in adult rats following oral, iv, and intratracheal administration. Also shown is whole body retention of ^{103}Pd in suckling rats following oral administration.

second component of the retention curve to the intercept indicated that the absorption was less than 0.5% of the initial dose. Retention of ^{103}Pd by the suckling rats following oral administration was similar to that of the adults; however, the amount absorbed and retained with time was significantly higher.

The amount of ^{103}Pd retained following intratracheal dosing was significantly higher than that for oral dosing and also significantly less than that for iv dosing. The greatest amount of ^{103}Pd retained with time occurred following iv administration. Approximately 10% of the initial iv dose was retained at 76 days when the whole body counting was discontinued.

Excretion

Radioactive counts of 24 hr. urine and feces samples from the rats receiving the ^{103}Pd orally showed that almost all of the ^{103}Pd was initially eliminated in the feces and only a trace amount was excreted in the urine (Figure 2). With iv administration, ^{103}Pd was eliminated both in the urine and feces in similar quantities. Toward the end of the study, urinary excretion exceeded fecal excretion.

Tissue Distribution

The distribution and concentration of ^{103}Pd was determined for different tissues following oral and iv dosing. Twenty-four hours after oral dosing, detectible quantities of ^{103}Pd were found only in the kidney and liver. The concentration in the kidney was much greater than that in the liver. Twenty-four hours after iv dosing, ^{103}Pd was found in all the tissues analyzed with the higher concentrations, in descending order, occurring in the kidney, spleen, liver, adrenal, lung, and bone, respectively.

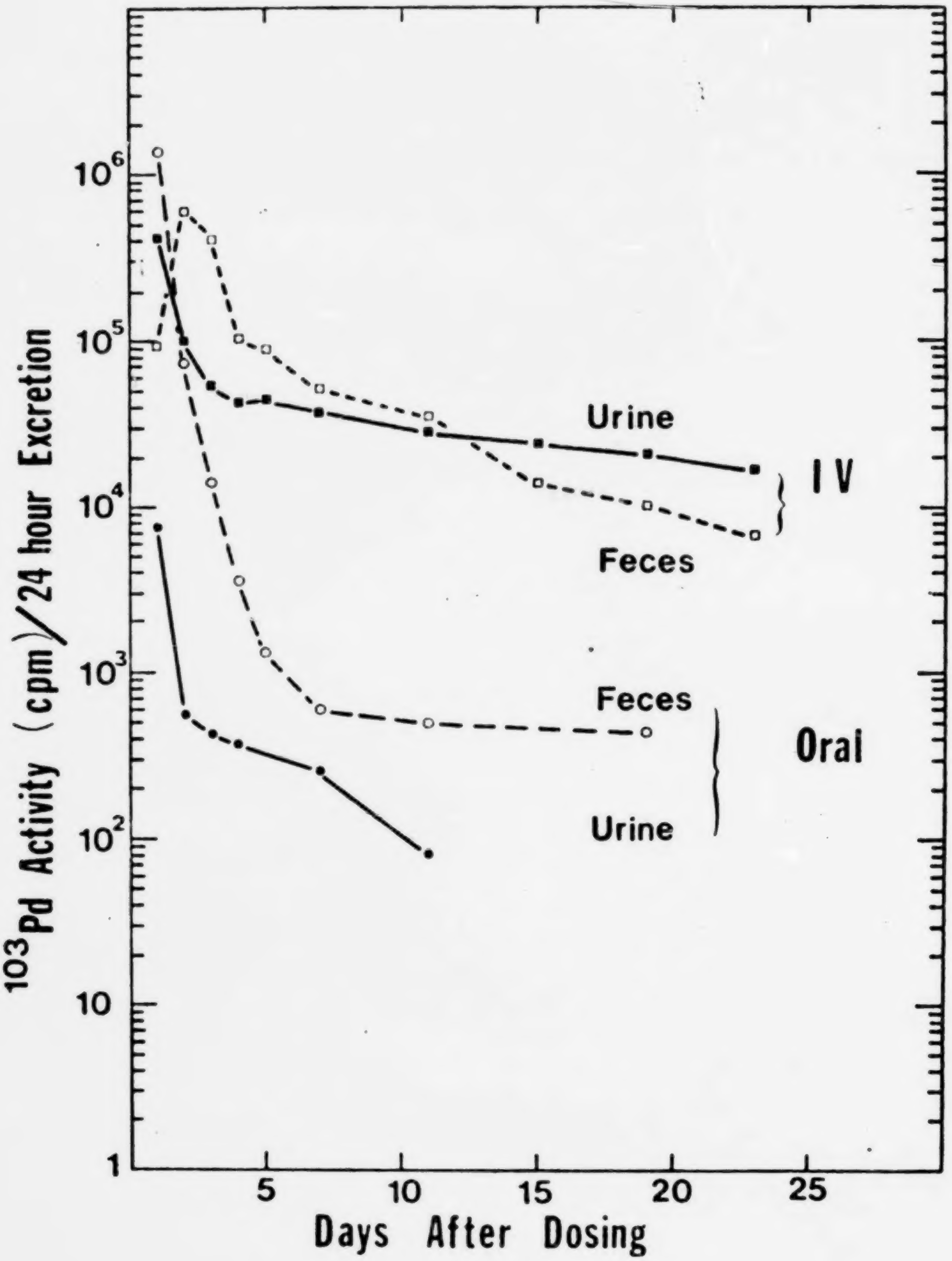

Fig. 2. Excretion of ^{103}Pd following iv and oral administration.

The rats used in the whole body retention study were sacrificed 104 days post-exposure and the tissues counted. No significant amount of ^{103}Pd was found in any of the tissues from the group receiving the oral dose. In the iv dosed rats, the higher concentrations of ^{103}Pd were found in the spleen, kidney, liver, lung, and bone. For the intratracheally dosed rats, the lung contained the most ^{103}Pd followed by the kidney, spleen, bone, and liver.

Maternal/Fetal Uptake

During the 24 hr. period, the pregnant rats excreted 44.2% of the initial iv dose. The amount excreted by the pregnant rats was higher than the amount excreted by the fasted adult male rats during the first 24 hr. period. The magnitude of the difference in ^{103}Pd concentration among the maternal organs and the fetuses is best shown by the counts per gram of tissue (Table 1).

The pattern of distribution and concentration of ^{103}Pd in maternal organs was similar to that previously found in the whole body iv experiment. Most of the fetuses (35) contained a small amount of ^{103}Pd, and the mean value for these fetuses is given in Table 1. However, radioactive counts for 17 fetuses from 5 litters was not significantly higher than background counts. The same pattern of results was obtained for the fetal livers. The amount of ^{103}Pd found in the fetuses indicated that Pd does not readily move across the placental barrier in the rat.

The retention of ^{103}Pd by the post-parturient dams and pups with time, following a single iv exposure is shown in Figure 3. It is evident

Table 1. ^{103}Pd in Maternal Organs and Fetuses

Tissue	Mean Counts/g
Maternal organ	
Blood	3,654
Lung	29,211
Liver	319,153
Kidney	588,479
Bone	18,351
Ovary	29,625
Placenta	58,321
Fetus	757
Fetal liver	1,429

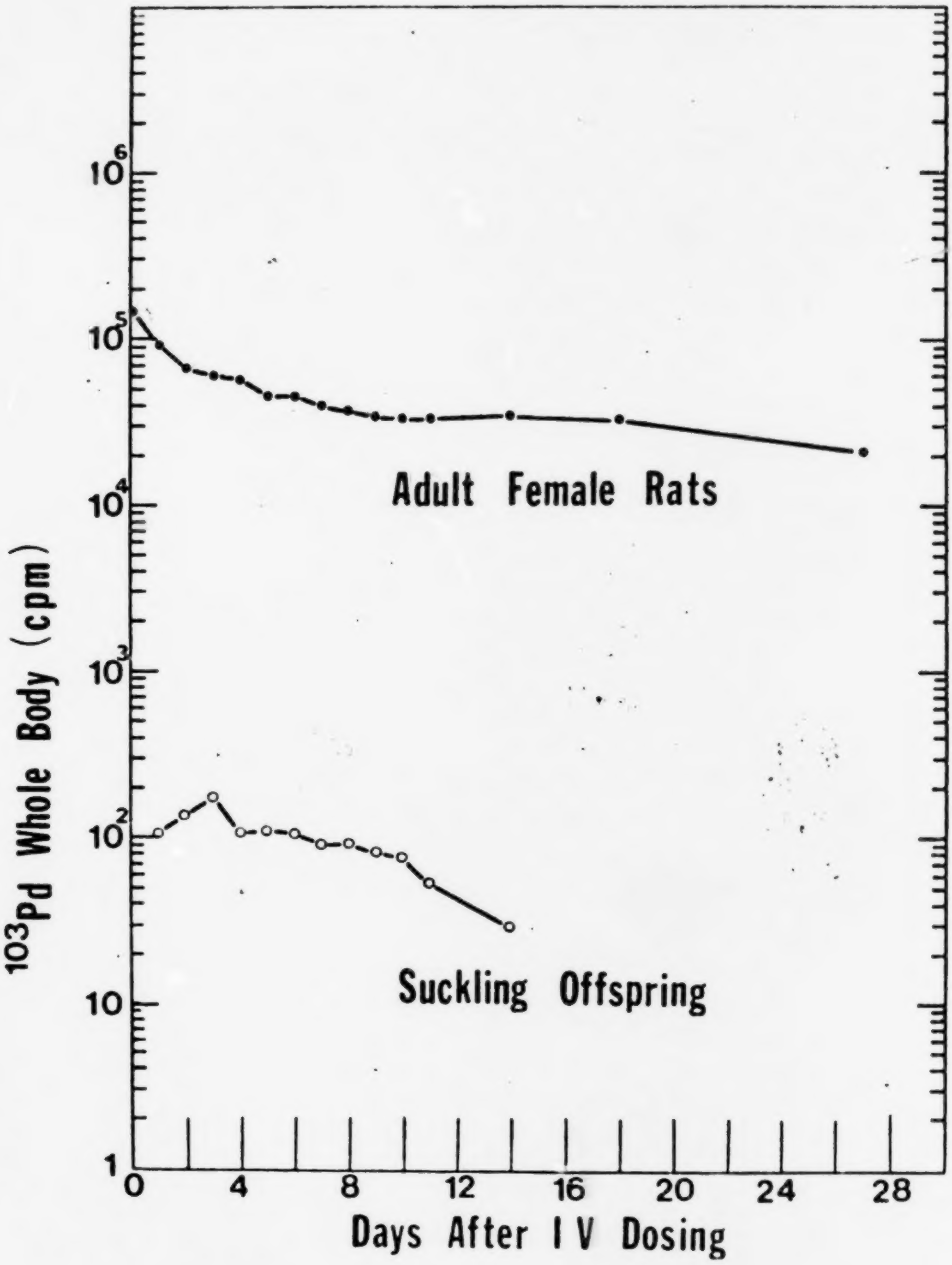

Fig. 3. Whole body retention of ^{103}Pd in nursing female rats following i.v. administration and uptake of ^{103}Pd in suckling young via the milk.

that a small amount of the ^{103}Pd was passed to the young via the milk. Twenty-five days after dosing of the dams, the suckling rats were sacrificed and lung, liver, kidney, bone, and spleen taken for analysis. A very small amount of ^{103}Pd (10-50 counts/gram tissue) was found in the tissues. The bone had the highest level of activity followed by the kidney, spleen, lung, and liver.

BIOLOGICAL FATE OF ^{191}Pt IN RATS FOLLOWING DIFFERENT ROUTES OF EXPOSURE

W. Moore, Jr., D. Hysell, W. Crocker and J. F. Stara

Because Pt may enter various media, the purpose of this study was to determine the significance of different routes of exposure upon retention, tissue distribution, and excretion. Placental transfer was determined following intravenous administration.

METHODS

Animals and Treatments

The outbred albino rats (Charles River CD-1 strain) used in this study were maintained on a commercial diet (Purina Lab Chow) and tap water *ad libitum* except where otherwise noted. The three treatment groups consisted of:

1. Intratracheal administration

Fourteen fasted male rats, 180-200 g, were anesthetized with pentobarbital sodium and placed in dorsal recumbency. The trachea was isolated through a ventral midline cervical incision and blunt dissection of the overlying musculature. ^{191}Pt (25 μCi in 0.1 ml saline) was injected intratracheally with a 1 cc tuberculin syringe and 5/8 in., 25 ga. needle. After the incision was closed, the animals were maintained in hanging wire cages for determination of whole body retention of ^{191}Pt.

2. Oral administration

Seventy-one fasted male rats, 180-200 g, were lightly anesthetized with ether and given 25 μCi of ^{191}Pt in 0.2 ml saline by stomach tube. Six rats were placed in metabolism cages for collection of 24 hour urine and feces samples to determine routes of excretion. Fifteen animals were used for whole body determinations. Ten rats were sacrificed on days 1, 2, 3, 7, and 14 after dosing to establish organ distribution of ^{191}Pt. Fifteen non-fasted suckling rats, approximately 30 g, were given a single dose of 25 μCi of ^{191}Pt by stomach tube. These animals were maintained for comparison with retention of Pt in adult rats.

3. Intravenous administration

Seventy male rats, 180-200 g, were given 25 μCi ^{191}Pt in 0.1 ml saline intravenously (iv) in a tail vein with a 1 cc tuberculin syringe and 5/8 in., 25 g needle. Six rats were placed in metabolism cages for collection of 24 hour urine and feces samples and 15 animals were used for whole body determinations. Ten rats were sacrificed on days 1, 2, 3, 7, and 14 after dosing to establish organ distribution of ^{191}Pt. An additional 15 pregnant rats (18th day gestation) were given 25 μCi ^{191}Pt iv and sacrificed 24 hours later for determination of placental transfer and organ distribution.

Sacrifice and Tissue Sampling

All rats were euthanatized with an overdose of chloroform anesthesia. Samples collected routinely for counting were blood, heart, lung, liver, kidney, adrenal, pancreas, abdominal fat, spleen, skeletal muscle, bone, brain, and testicle from males, ovary from females. In the pregnant females, 4 placentas, 4 fetuses, and a pooled sample of fetal livers were also saved.

Radioactive Determinations

A carrier free solution of $^{191,193}Pt^{+4}$ in 1M HCL was used for this study. The ^{191}Pt isotope comprised at least 50% of the total radioactive Pt and the 0.529 MeV gamma of ^{191}Pt was counted in the radioactive determinations. ^{191}Pt has a 3-day half-life. Immediately after dosing, whole body counts were made on all animals used in the retention studies. The animals were counted daily for the first few days and then every other day for the duration of the experiment. A 200-channel gamma spectrometer with a 5 in. NaI (Tl) crystal was used for whole body counts. Tissue, urine, and feces samples were counted in a well-type refrigerated scintillation spectrometer.

RESULTS

Whole Body Retention

Whole body retention of ^{191}Pt following a single dose was affected significantly by the route of administration. The percent of ^{191}Pt retained with time following 3 different routes of administration is presented in Figure 1. Following oral dosing, the total net gastrointestinal excretion was extremely high resulting in a rapid decline of the retention curve to less than 1% at the end of 3 days. Retention of ^{191}Pt by suckling rats following oral administration was similar to the adults although the amount retained at 24 hours was higher (14.7% for the suckling rats vs. 7.4% for the adults). The difference in whole body retention probably is due to difference in the rate of movement of the ^{191}Pt through the gastrointestinal tract.

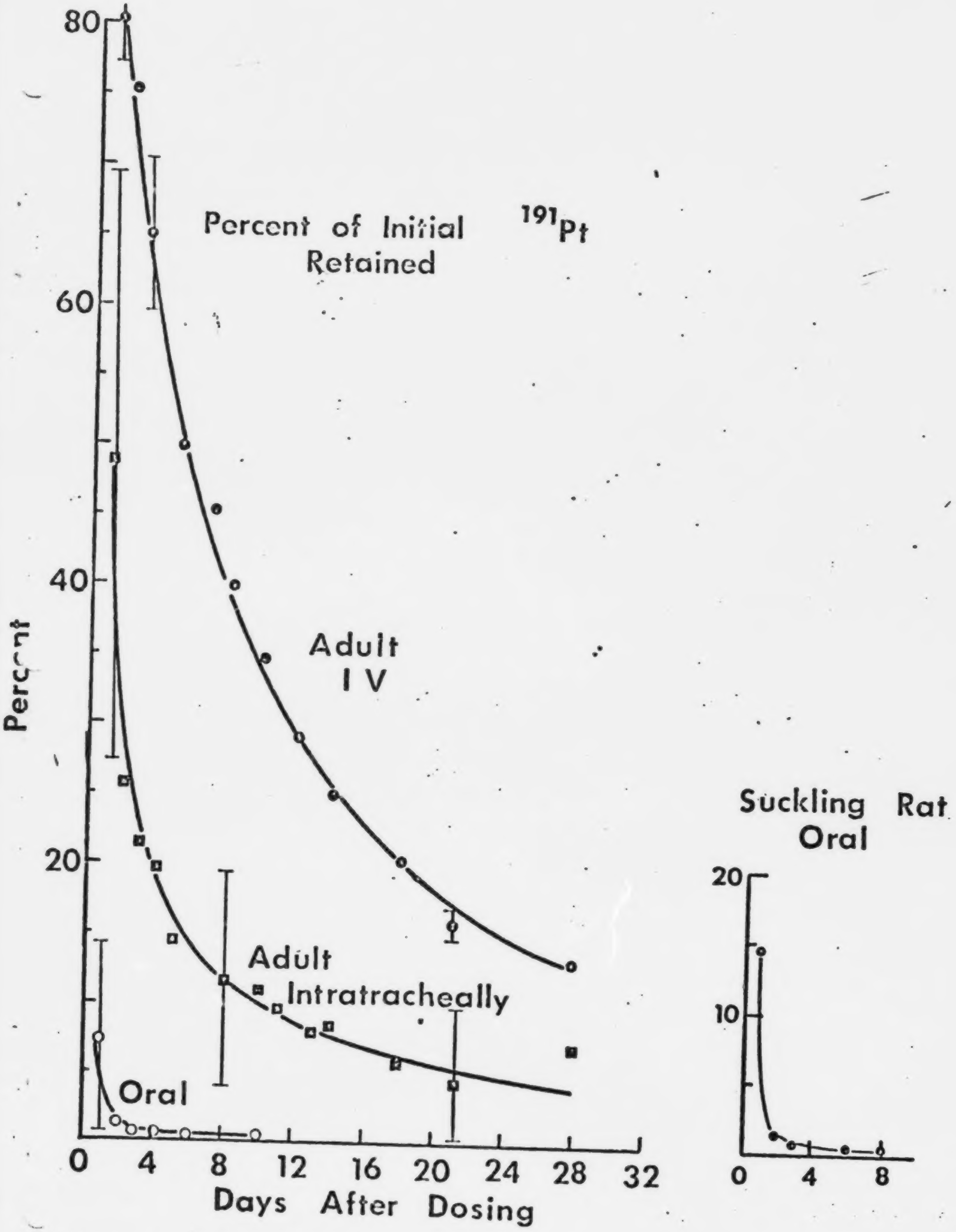

Figure 1. Whole body retention of ^{191}Pt in adult rats following oral, iv, and intratracheal administration. Also shown is whole body retention of ^{191}Pt in suckling rats following oral administration.

The amount of ^{191}Pt retained in the body following intratracheal dosing was significantly higher than for oral dosing. The excretion of approximately 50 percent of the initial dose during the first 24 hours is attributed to mucociliary and alveolar clearance. Whole body retention of ^{191}Pt was the highest following iv dosing; the short half-life precluded an accurate determination of the biological half-life for this metal.

Excretion

Radioactive counts of 24 hour urine and feces samples from rats receiving ^{191}Pt orally indicated that almost all of the ^{191}Pt was eliminated in the feces and only a small amount excreted in the urine (Figure 2). These values support the whole body data which showed that total net gastrointestinal absorption was low. Following iv administration, ^{191}Pt was excreted in both the urine and feces. The urine contained a greater quantity of the ^{191}Pt.

Tissue Distribution

The distribution and concentration of ^{191}Pt was determined for different organs as a function of time following oral and iv dosing. After oral dosing, the kidney and liver contained the highest concentrations of ^{191}Pt. The amount of radioactivity found in the other organs was not significantly higher than background. The amount of ^{191}Pt found in selected tissues and the percent of the initial dose per gram following iv dosing are presented in Table 1. Most of the tissues did not contain levels of ^{191}Pt appreciably higher than that found in blood. However, the fraction of ^{191}Pt in the plasma that is in an "available" form for movement into the various tissues was not determined. The large amount

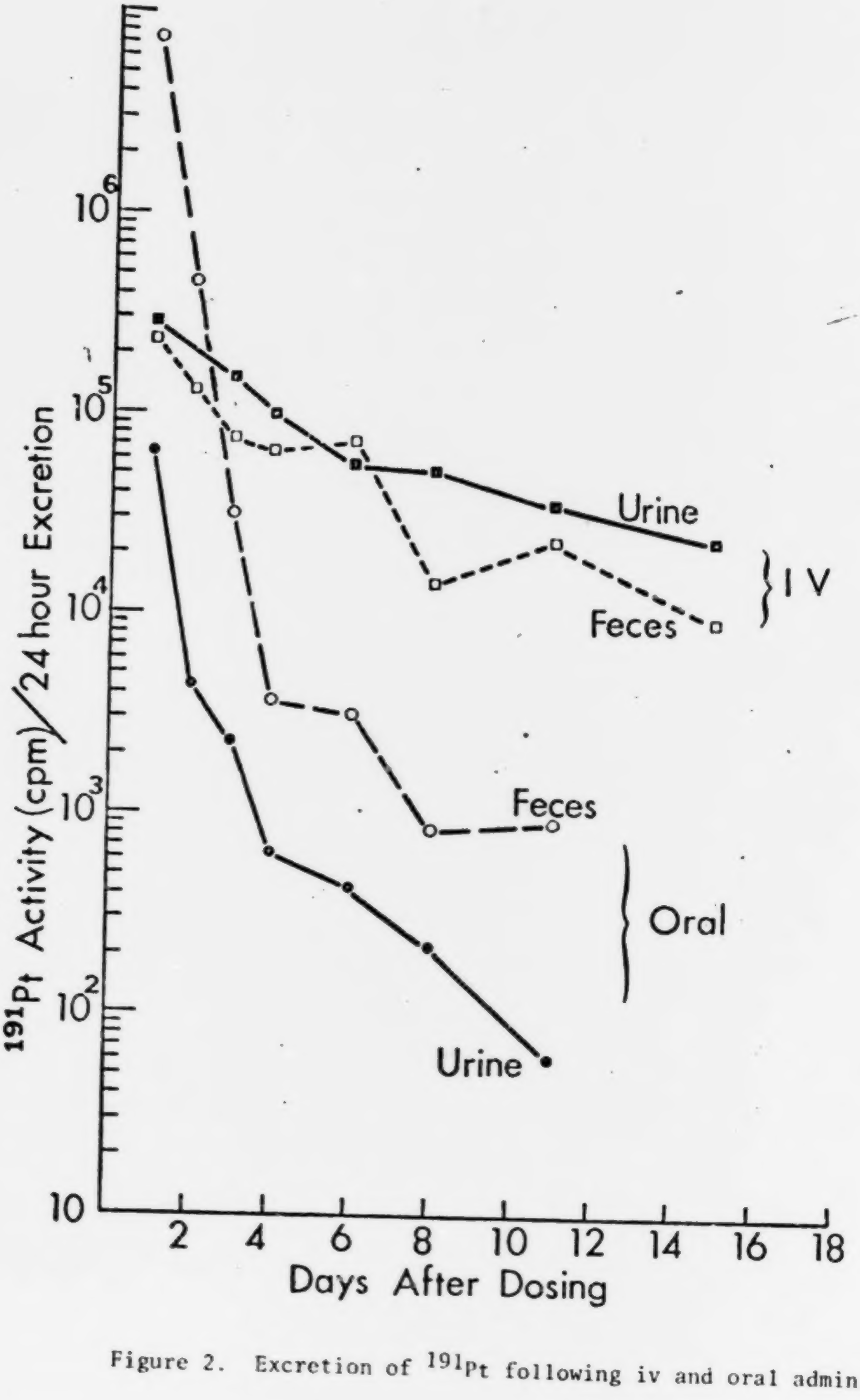

Figure 2. Excretion of ^{191}Pt following iv and oral administration

Table 1. ^{191}Pt Present in Rats Following A Single Intravenous Dose

Tissue	1 day		2 days		7 days		14 days	
	c/g Wet Weight	% Per Gram	c/g Wet Weight	% Per Gram	c/g Wet Weight	% Per Gram	c/g Wet Weight	% Per Gram
Blood	22,147	0.91	19,732	0.81	12,774	0.52	7,921	0.32
Heart	11,819	0.48	12,201	0.50	8,805	0.36	4,593	0.19
Lung	18,432	0.75	16,139	0.66	11,180	0.46	5,770	0.24
Liver	36,848	1.51	31,274	1.28	25,732	1.05	4,733	0.19
Kidney	162,227	6.65	160,656	6.59	138,101	5.66	30,195	1.24
Spleen	41,085	1.68	45,840	1.89	55,764	2.29	20,973	0.86
Pancreas	22,208	0.91	19,487	0.80	14,802	0.60	3,973	0.16
Bone	13,146	0.53	12,800	0.52	8,932	0.37	5,440	0.22
Brain	1,150	0.05	2,485	0.10	595	0.02	265	0.01
Fat	4,487	0.18	4,501	0.18	3,201	0.13	429	0.02
Testis	4,186	0.17	6,540	0.27	3,873	0.16	1,431	0.06
Adrenal	45,439	1.86	42,363	1.74	26,667	1.09	6,190	0.25
Muscle	4,798	0.19	4,671	0.19	3,441	0.14	2,146	0.09
Duodenal Segment	12,725	0.52	6,044	0.25	4,031	0.16	1,410	0.06

of ^{191}Pt found in the kidney suggests that this organ accumulates this element. Concentrations higher than the blood values were also found in the liver, spleen, and adrenal. The relative low count for the brain indicated that ^{191}Pt was transferred through the blood-brain barrier only to a limited extent.

Maternal/Fetal Uptake

Fifteen pregnant rats (18th day gestation) were given 25 pc Ci ^{191}Pt intravenously and sacrificed 24 hours later to determine placental transfer. During the 24 hour period, the pregnant rats excreted 18.8 percent of the initial dose. The amount excreted by the pregnant rats was approximately the same as the amount (19.3 percent) excreted by the adult male rats during the first 24 hours period. The concentration of ^{191}Pt per gram for different maternal tissues and fetuses is given in Table 2.

The data indicated that there was some transplacental passage of 191Pt, however, there appeared to be placental binding or accumulation. ^{191}Pt was present in all the fetuses (60) counted. The hemochorial placental barrier of rats is more easily traversed than the more complex placental barriers found in other species of experimental animals.

Table 2. ^{191}Pt in Maternal Organs and Fetuses

Tissue	Mean Counts/g	% of Dose Per Gram
Blood	10,568	0.35
Lung	17,981	0.60
Liver	43,375	1.44
Kidney	127,064	4.22
Bone	9,193	0.30
Brain	792	0.02
Ovary	14,639	0.49
Placenta	27,750	0.92
Fetus	432	0.01
Fetal Liver	1,421	0.05

THE ACUTE TOXICITY OF PALLADIUM CHLORIDE AND PLATINUM CHLORIDE

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W. Crocker, D. Hysell, W. Moore and J. Stara

As part of the comprehensive evaluation of the toxicity of catalytic emission products, acute toxicity studies of Pd and Pt chlorides were initiated. This data provides a reliable and inexpensive first estimate of the toxicity as related to dose.

METHODS

The outbred albino rats (Charles River CD-1 strain, 200-300g) used in these studies were maintained on a commercial diet (Purina Lab Chow) and tapwater *ad libitum* except where otherwise noted. Rabbits were obtained from a local supplier and fed a commercial diet (Purina Rabbit Chow) and tapwater ad libitum.

A. Toxicity Studies of Pd and Pt

Animals were given a single dose of $PdCl_2$ or $PtCl_4$ by one of the following routes: 1) orally (po); 2) intravenously (iv); 3) intraperitoneally (ip); 4) intratracheally (itr). All solutions were prepared in saline with no pH adjustment.

Four groups (10 animals/group) of rats were given Pd or Pt in the drinking water and appearance, body weight and water consumption noted. The concentrations used were 92 and 184 ppm K_2PdCl_4 and 235 and 470 ppm K_2PtCl_4.

RESULTS

A. Palladium Toxicity

Using the method of Diechman and LeBlanc, the approximate LD50 of $PdCl_2$ was determined for iv, ip, itr, and po routes of administration. The results are shown in Table 1.

Table 1. Acute Lethal Toxicity of PdCl

Species	Approx. LD50	Route
Rat	5 mg/kg	iv
Rat	70 mg/kg	ip
Rat	200 mg/kg	po
Rat	6 mg/kg	itr
Rabbit	5 mg/kg	iv

Marked differences in the approximate LD50 were noted among the different routes of administration, ranging from 5 mg/kg for iv to greater than 200 mg/kg for po.

Using the more precise method of Litchfield and Wilcoxon,[2] the iv and ip LD50 (14 days) were determined. The iv LD50 (14 days) was calculated to be 3.0 mg $PdCl_2$/kg with 95% confidence limits of 2.57-3.49. The slope was found to be 1.43 with a 95% confidence limits of 1.15-1.77. The $(CHI)^2$ test indicated that the data were not significantly heterogenous. Following ip administration, the LD50 was calculated to be 123.0 (91.1-166.1) mg $PdCl_2$/kg with a slope of 1.84 (1.04-3.27). No significant heterogenicity was noted.

Following acutely toxic iv doses of $PdCl_2$, death occurred very rapidly, with a sharp threshold such that if exitus did not occur within 5-10 minutes, the animals (both rats and rabbits) survived the 14 day experimental period. Clonic and tonic convulsions were noted in rats and rabbits. Following ip injection, necropsy findings indicated a chemical type "burn" of the viscera in animals dying within 24 hrs. Gross pathologic examination of ip-dosed survivors at 14 days showed prominent peritonitis with numerous visceral adhesions.

A limited number of rats from the intravenous and intraperitoneal studies were housed in metabolism cages and several toxicometric parameters were measured during the 14 days observation period. Survivors of an acutely toxic iv dose of $PdCl_2$ exhibited a 25 per cent decrease in water intake and urine excretion. Following intraperitoneal dosing a 7 per cent reduction in body weight was observed with up to 80 per cent reduction in food intake. Water intake was markedly reduced initially and then returned to control levels or above. Proteinuria was noted in all animals following both routes of administration. Elevated urinary ketone bodies were observed in some animals following both routes of dosing.

In order to ascertain the effect of chemical form on toxicity, the LD50 of K_2PdCl_4 and $(NH_4)_2\ PdCl_4$ were determined (Table 2). The LD50 when expressed in micromoles of Pd was very similar for the 3 chemical forms.

In two groups of rats maintained for 33 days on drinking water containing 92 ppm and 194 ppm K_2PdCl_4, respectively, there were no abnormalities noted in general appearance, body weights or urinalysis.

Table 2. Intravenous LD50 for Pd Compounds Using the Litchfield and Wilcoxon Method

Compound	LD50 mg/kg (95% Confidence)	Slope (95% Confidence)	LD50 μM/kg
$PdCl_2$	3.0 (2.6-3.50)	1.43 (1.1-1.8)	16.9
K_2PdCl_4	6.4 (6.0-6.8)	1.14 (0.83-1.2)	19.6
$(NH_4)_2PdCl_4$	5.6 (4.9-6.4)	1.31 (0.96-1.8)	19.7

B. Platinum toxicity

The results of a preliminary range finding study on the acute toxicity of iv $PtCl_4$ in rats is given in Table 3. The high incidence of mortality at the lowest dose precluded determination of the LD50 (14 days). However, the lowest dose would appear to be a reasonable approximation.

Table 3. Acute Intravenous Toxicity of $PtCl_4$ in Rats

$PtCl_4$ Dose mg/kg	No. of Rats per group	Cumulative Deaths	% Mortality
41.4	10	10	100
36.7	10	9	90
31.4	10	9	90
26.2	10	4	40

In two groups of rats maintained for 23 days on drinking water containing 235 ppm and 470 ppm K_2PtCl_4, respectively, there was a decrease in weight gain and water consumption. For the high dose level the weight gain decreased 14.7% and the water intake decreased 32.3%. No gross pathological changes were found at necropsy. Additional studies are currently in progress on Pt toxicity.

In Vitro Studies

In vitro protein binding studies were performed with Pd and Pt chlorides ($PdCl_2$ and $PtCl_4$), using the Toribara ultracentrifugation technique[3] at concentrations up to 200 μg of compound/ml, using whole plasma or plasma equivalent albumin. Protein binding was greater than 99 percent at all concentrations. Temperature and pH were found not to affect binding.

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IN VITRO EFFECT OF VARIOUS SULFATE COMPOUNDS ON SUCCINATE-DEPENDENT RESPIRATION

V. Finelli, M. Karaffa, M. Richards, L. McMillan and S. D. Lee

The use of catalytic converters to control hydrocarbons and carbon monoxide in the automobile exhaust emissions resulted in an increased output of sulfate(s).[1] This, along with possible emissions of noble metals from the converter, prompted us to test comparative toxicity of the various sulfates in an enzyme system. Succinate dependent respiration was tested in rat liver slices incubated in Krebs-Ringer phosphate buffer and in liver homogenate incubated in .011M phosphate buffer, pH 7.4. A Clark-type oxygen electrode attached to a YSI Model 53 Biological Oxygen Monitor (Yellow Spring Instrument Co.) was used to measure the O_2-uptake.[2,3] We tested the effects of various sulfates such as cadmium, palladium, manganese, magnesium, calcium, sodium, and ammonium on the system. The results indicated that the sulfate ion in tissue slices or in homogenate did not effect the respiratory chain. However, among the cations, Cd^{++} appeared to be the most potent inhibitor (Figure 1). Cadmium inhibited the O_2-uptake by approximately 50% at 2×10^{-7}M and 100% at 3.3×10^{-5}M. Other cations did not show inhibitory effects at similar concentrations. To achieve a 50% inhibition by $PdSO_4$ more than 10^{-3}M was required. Cadmium ion, a known potent inhibitor of the mitochondrial respiratory chain,[4] was utilized in this experiment as a reference toxicant. Cadmium sulfate was found to be at least 5,000 times more toxic to the respiratory chain than $PdSO_4$. As expected, other cations such as Mn^{++}, Mg^{++}, Ca^{++}, Na^{++} were not inhibitory at concentrations up to 10^{-3}M, but appeared to have a slight stimulatory effect.

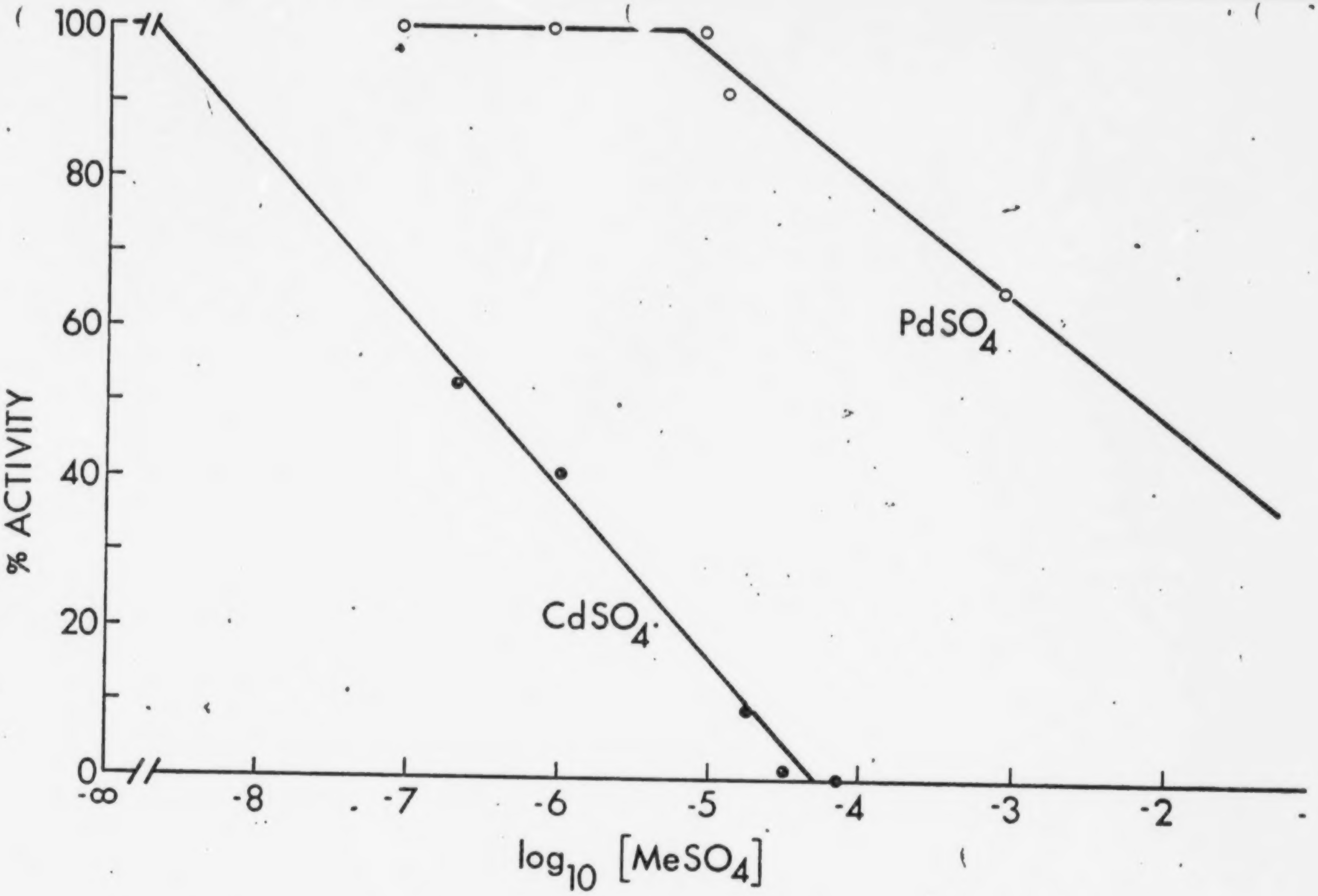

Figure 1. Effect of $CdSO_4$ and $PdSO_4$ on Succinate dependent O_2-uptake in rat liver homogenate.

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EFFECT OF NOBLE METAL COMPOUNDS ON PROTEIN SYNTHESIS IN VARIOUS ORGANS OF RATS

S. D. Lee and R. M. Danner

Experiments were conducted to detect early biochemical effects of intragastric administration of noble metal compounds ($PdCl_2$ and $Pt[SO_4]_2$) on protein synthesis in various organs as determined by the rate of incorporation of ^{14}C-leucine. Experimental animals (rats) were given $PdCl_2$ (1 mg/kg body weight) 24 hr before sacrifice. Control animals were given saline solution. All rats (control and treatment groups) received an injection of ^{14}C-leucine (140 μCi/kg body weight) through the tail vein and were allowed to metabolize for 1 hr before sacrifice. The ^{14}C-content of purified protein in liver, kidney, lung, heart, and blood serum were examined.

Each of the excised organ samples was homogenized with 0.25 M sucrose (3:1 v/w). An aliquot of the homogenate was used to precipitate protein with 10 percent trichloroacetic acid v/v. The precipitate was washed twice with 5 percent trichloroacetic acid v/v and then twice with 95 percent ethanol. The concentration of protein was determined by the Biuret method. Radioactivity levels were measured in a Packard liquid scintillation spectrometer. The observed values were expressed in terms of dpm/mg protein and percent alteration with reference to control.

As can be seen in Table 1, no change was observed in the kidney and lung, and there was only a slight decrease in the liver. However, there was a marked increase in ^{14}C-leucine incorporation into the heart and blood serum protein. The increases were 137 percent and 49 percent in heart and blood serum, respectively.

Table 1. EFFECT OF PdCl$_2$ ON ^{14}C-LEUCINE INCORPORATION INTO PROTEIN

Item	Liver		Kidney		Lung		Heart		Blood serum	
	dpm/mg protein	No. of animals	dpm/mg protein	No. of animals	dpm/mg protein	No. of animals	dpm/mg protein	No. of animals	dpm/mg protein	No. of animals
Control	1,484.0	4	1,708.0	4	1,566.5	4	955.0	4	1,877.3	3
Experimental	1,361.8	4	1,728.2	5	1,540.6	5	2,265.0	4	2,796.5	4
Percent Change	-8.0	-	+1.2	-	-1.7	-	+137.2	-	+49.0	-

Table 2. EFFECT OF Pt(SO$_4$)$_2$ ON ^{14}C-1-LEUCINE INCORPORATION INTO PROTEIN

Dose (mg/kg of body wt) and percent change	Liver		Kidney		Lung		Heart		Brain	
	cpm/mg protein*	No. of animals	cpm/mg protein*	No. of animals	cpm/mg protein*	No. of animals	cpm/mg protein*	No. of animals	cpm/mg protein*	No. of animals
0 mg/kd	1,056	6	2,332	6	1,732	6	1,355	6	882	6
0.5 mg/kg	1,374	4	2,807	5	1,911	5	1,356	5	1,142	5
Percent change	+30.1	-	+16.9	-	+10.3	-	0	-	+29.5	-
1.0 mg/kg	1,088	4	2,477	4	2,239	4	1,326	4	1,111	4
Percent change	+3.0	-	+6.2	-	+22.7	-	-2.1	-	+26.0	-
5.0 mg/kg	1,110	4	2,331	4	3,627	4	1,233	4	949	4
Percent change	+5.0	-	0	-	+109.4	-	-9.0	-	+7.0	-

*Corrected for organ weight.

Rats given 0.5, 1.0, and 5.0 mg/kg body weight of $Pt(SO_4)_2$ exhibited a different pattern of ^{14}C-leucine incorporation into protein as depicted in Table 2. The patterns of ^{14}C-l-leucine incorporation into protein of five organs were examined. The most pronounced change was observed in the lung, where a definite dose-response was observed with increasing concentration: incorporation of ^{14}C-l-leucine rose 10.3 percent for 0.5 mg/kg, 22.7 percent for 1.0 mg/kg, and 109.4 percent for 5 mg/kg body weight, respectively.

The incorporation of ^{14}C-l-leucine in kidney showed a reverse trend: +16.9 percent for 0.5 mg/kg, 6.2 percent for 1.0 mg/kg, and no change for 5 mg/kg body weight, respectively. The changes in the brain showed a similar pattern to the kidney. There was a 30 percent increase at 0.5 mg/kg body weight for liver, and no other apparent changes were indicated. Treatment with 5.0 mg/kg body weight of $Pt(SO_4)_2$ resulted in a 9 percent decrease. Increases of about 30 percent and 26 percent for the 0.5 mg and the 1.0 mg/kg levels were observed, respectively. Apparently, $Pt(SO_4)_2$ at the concentrations used in this study did cause a significant disruption in protein synthesis in organs tested.

DERMAL IRRITANCY OF SEVERAL PALLADIUM, PLATINUM, AND LEAD COMPOUNDS AND OF METHYLCYCLOPENTADIENYL MANGANESE TRICARBONYL

K. I. Campbell, E. L. George, L. L. Hall, and J. F. Stara

A necessary aspect of the general toxicologic characterization of potential environmental pollutants is the evaluation of dermal irritancy. A series of such tests were performed on several palladium (Pd) and platinum (Pt) compounds because of their relevance to catalytic automotive emission control devices, and on two lead (Pb) compounds and the gasoline antiknock additive, methylcyclopentadienyl manganese tricarbonyl (MMT).

The test procedure used was essentially that in standard use by the National Institute of Occupational Safety and Health,[1,2,3] a modification of the official Food and Drug Administration procedure.[4] In each test, six healthy, male, albino rabbits weighing 2 to 3 kg were used. Up to seven pairs of sites (2 x 2 cm) were used on the closely clipped dorsolateral aspects of the trunk of each animal, with the sites on the right side abraded and those on the left intact. Test materials in the solid (powder) state (0.1-g per site) were mixed with about 0.1 ml deionized water and spread over the site; liquid materials were applied directly in 0.1-ml quantities. Each application was covered immediately with a gauze patch and further secured with tape (and overwrap in one test); a leather restraining harness was also used. After 24 hr, harnesses and coverings were removed, and test sites were washed with mild soap, rinsed, and dried. The skin reactions were evaluated and scored and again 48 hr later. Skin reactions were evaluated and scored using a grading system summarized in Table 1. The assigned rating was calculated as the average of the means from the 24- and 72-hr scores for the test group; intact and abraded skin was rated separately (Table 2). Ratings were interpreted according to the scheme summarized in Table 3.

Table 4 shows the materials tested, the dermal irritancy (intact skin) and cellular toxicity (abraded skin) responses observed, and the corresponding interpretations. Results were interpreted conservatively, that is, based on the test in which the most severe responses were observed. Many of the test materials caused a delayed healing of the abrasion lines themselves, in addition to or regardless of the standard response criteria.

The severity of response to some of the compounds which were tested more than once was quite variable. Skin character and hair growth patterns among rabbits in the specified weight range were somewhat variable, and these could be factors in irritancy responses and evaluations. We recommend selection of rabbits for uniformity on these additional criteria. Close but gentle (atraumatic) clipping in preference to shaving, and over-wrapping in preference to taping to secure the patches, are also recommended. In addition to tests for dermal irritancy, tests for sensitization should also be performed. Sensitizations may be far more serious or chronic than direct irritation. They may develop at lower and more common levels of exposure, and opportunity for development may be greater by virtue of extended or repeated exposure by ingestion and inhalation as well as cutaneous contact.

For comparison, one of the authors (KIC) applied $(NH_4)_2\ PdCl_4$ and $(C_3H_5PdCl)_2$ to the intact inside forearm skin in a manner similar to that used in the rabbit tests. The 24 hr reactions were read as 2() and 2(+), on the scale of 4 used in the rabbits, for $(NH_4)_2\ PdCl_4$ and $(C_3H_5\ PdCl)_2$, respectively. These scores represented somewhat different degrees of severity of erythema and edema. The $(NH_4)_2\ PdCl_4$ reaction abated after removal of the patch after 24 hr so that only a faint brown stain of the epidermis remained on the third day. The edema reaction to $(C_3H_5\ PdCl)_2$ appeared to abate also, but residual effects were prolonged. A definite brown parchment-like lesion remained for about two weeks, and a residual erythema remained for about five additional weeks. Both test sites itched a little during the first day, but not after removal of the material. There was no erythematous reaction to the patches' adhesive material, as sometimes occurred in the rabbit tests.

Table 1. EVALUATION OF SKIN REACTIONS TO TEST MATERIALS

Reaction	Grade value and designation	
	Intact skin	Abraded skin
No. irritation	0, nonirritant	0, nontoxic
Erythema (regardless of degree)	1, mild irritant	1, mild cellular toxin
Erythema and edema confined to test area	2, irritant	2, cellular toxin
Erythema and edema extending beyond test area	3, strong irritant	3, strong cellular toxin
Eschar (deep reaction involving dermis)	4, corrosive	4, corrosive

Table 2. EXAMPLE CALCULATION OF TEST RATING

Item	Intact skin reaction (dermal irritancy)*				Abraded skin reaction (cellular toxicity)+			
	24 hr	72 hr	Total	Mean	24 hr	72 hr	Total	Mean
Animal Number:								
1	1	1	2	1.0	2	3	5	2.5
2	0	1	1	0.5	1	2	3	1.5
3	2	1	3	1.5	2	2	4	2.0
4	1	0	1	0.5	2	1	3	1.5
5	1	2	3	1.5	2	2	4	2.0
6	0	1	1	0.5	1	1	2	1.0
Total:	-	-	-	5.5	-	-	-	10.5
Average:		-	-	0.9	-	-	-	1.8

*Dermal irritation rating for intact skin = 5.5÷6 = 0.9. In this example, the material is a nonirritant.

+Primary irritation rating for abraded skin = 10.5÷6 - 1.8. In this example, the material is a mild cellular toxin.

Table 3. INTERPRETATION OF SKIN TEST RATINGS

Rating		Interpretation
Intact skin	Abraded skin	
0 - 0.9	-	Nonirritant; probably safe for contact with intact human skin.
1 - 1.9	-	Mild irritant; may be safe for use, but appropriate protective measures are recommended during contact.
2 - 4	-	Too irritating for human skin; avoid contact.
-	0 - 0.9	Nontoxic to cellular components of abraded skin; probably safe for human skin contact.
-	1 - 1.9	Mild cellular toxins; may be safe for abraded skin contact, provided that protective measures are employed.
-	2 - 4	Cellular toxins too irritating for abraded skin contact; avoidance of contact is advised.
		Mixed reactions
0 - 0.9	0 - 0.9	Safe for human skin contact.
-	1 - 1.9	Safe for contact with intact human skin; may be safe for abraded skin contact when protection is maintained.
-	2 - 4	Safe for intact human skin; contact with abraded skin should be avoided.
1 - 1.9	1 - 1.9	May be safe for contact with intact and abraded skin when protection is maintained.
-	2 - 4	May be safe for contact with intact human skin when protection is maintained, but contact with abraded skin is to be avoided.
2 - 4	2 - 4	Unsafe for contact with intact and abraded human skin; avoid contact.

Material tested	Severity rating*		Interpretation+
	Intact skin (irritancy)	Abraded skin (cellular toxicity)	
ionized water negative control)	0	0	Safe for human skin contact.
acial acetic acid ethanoic) acid Positive control)	2.6	3.2	Unsafe for human skin contact.
tassium chloropalladite, $_2PdCl_4$	0 (0)	1.6 (1.9)	Safe for intact human skin; may be safe for abraded skin when protection is maintained.
tassium chloropalladate, $_2[PdCl_6]$	0 (0)	1.6 (2)	Safe for intact human skin; abraded skin contact should be avoided.
lladium chloride, dCl_2	0 (0.1)	0.6 (1)	Safe for intact human skin; may be safe for abraded skin when protection is maintained.
lylpalladium chloride imer, $(C_3H_5PdCl)_2$	0.8	1.8	Unsafe for human skin contact.
chlorodiamine palladium)Trans, $Pd(NH_3)_2.Cl_2$	0 (0)	0.2 (0.5)	Safe for human skin contact.
monium chloropalladite, $NH_4)_2PdCl_4$	1.5 (3.1)	2.5 (3.7)	Unsafe for human skin contact.
monium chloropalladate, $NH_4)_2PdCl_6$	2.8	3.2	Unsafe for human skin contact.
lladium monoxide, PdO	0	0	Safe for human skin contact.
atinum (II) dichloride, tCl_2	0.2	0.6	Safe for human skin contact.
atinum (IV)tetrachloride, tCl_4	1.8 (2.7)	2.6 (3.8)	Unsafe for human skin contact.
atinum (IV)dioxide, O_2	0	0	Safe for human skin contact.
ad chloride, Cl_2	0	0	Safe for human skin contact.
ad monoxide O	0	0.1	Safe for human skin contact.
hylcyclopentadienyl nganese tricarbonyl (MMT)	0.1	0.8	Safe for human skin contact.

*ing in parentheses indicates the most severe test result where there was more than one s, those without indicate the single test rating or an average of 2 or 3 test ratings.

ased on the most severe or single test result.

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DERMAL ABSORPTION OF ^{191}PLATINUM^{+4} IN HCl SOLUTION

K. Campbell, E. George, W. Moore, W. Crocker, and F. Truman

In conjunction with tests of dermal irritancy of platinum (Pt) compounds, an experiment to assess transcutaneous absorption of ionic Pt was performed. In each of 5 rabbits, 10 µl of a solution containing $^{191}Pt^{+4}$ in 0.5 M HCl was spread over a closely clipped, 1-cm square area of dorsal skin in the scapular region. The nuclide dose was 8.36 µCi; a Packard gamma scintillation spectrometer (Model 5375) was used for counting. Samples of blood before application and at 4, 24, 48, and 72 hr post-application, and 72 hr terminal samples of skin (incorporating the site of application), liver, and kidney were counted. Counts were corrected for background and decay, expressed as counts per minute per g of sample (except for the skin specimen, for which only total count was pertinent), and the fraction of the original applied dose was calculated.

Results showed that at the 72-hr terminal period, on the average, 53.41 percent of the original dose was in or on the skin at the site of application and that very small fractions appeared in the blood or in the tissues. Of the sequential blood samples, the earliest (at 4 hr post-application) contained by far the greatest fraction of the applied dose (0.0074 percent); subsequent samples contained less than one-tenth as much. Among the tissues at sacrifice, the concentration of activity in kidney was about 2.7 times that in liver and 14.3 times that in blood. The results are summarized in Table 1. Data from this experiment do not permit conclusions as to total amounts absorbed versus amounts

Table 1. TISSUE LEVELS OF ^{191}Pt ACTIVITY FOLLOWING DERMAL APPLICATION OF ^{191}PLATINUM^{+4} IN HCL SOLUTION

Specimen	Counts per minute/g (mean)	Proportion of dose applied, decimal, fraction x10^{-6} Mean	Range	Remarks
Blood:				
Pretreatment	0	0	0 - 0	n=5
Post-treatment:				
4 hr	92.4	74.0	0 - 240	"
24 hr	1.4	1.24	0 - 3.2	"
48 hr	6.8	6.60	0 - 30	"
72 hr (terminal)	2.1	1.82	0 - 8	"
Skin, terminal	594,493*	534,100	274,000 - 732,000	"
Liver, terminal	11.35	10.25	3 - 16	n=4
Kidney, terminal	30.3	27.0	6 - 48	n=5

*Total, based on entire skin sample.

lost from the skin, the fractional distribution to other tissues, and the amounts excreted; they do suggest early minor transcutaneous absorption, with distribution to blood, liver, and kidney. There was no visible sign of dermal irritation at the site of application.

OCULAR IRRITATION OF TWO PALLADIUM AND TWO PLATINUM COMPOUNDS IN RABBITS

D. Hysell, S. Neiheisel, and D. Cmehil

The test was performed as outlined in the Code of Federal Regulations[1] (Title 21, part 191.12, revised as of April 1, 1973). Two groups of six albino rabbits having no known ocular abnormalities were restrained and 10.0 mg of the test material was deposited on the surface of the right eye. The left eye was maintained as a control. The animals were examined for ocular inflammation 24, 48, and 72 hr following application of the material.

In the case of PdO (Table 1), no reaction was noted in any of the six rabbits. In one animal, the test material was still present in the conjunctival sac at the end of 72 hr, but was completely covered with a thick mucous material.

All six animals receiving PdCl showed a severe corrosive type lesion of the conjunctiva with severe inflammation of the cornea and anterior chamber of the eye (Table 1). This was noted at 24 hr and persisted throughout the test period.

None of the animals receiving the platinum compounds showed any ocular irritation.

These results indicate that at the dosage levels used, PdCl was a severe irritant, and PdO was not. Neither of the platinum compounds were irritating.

Table 1

Compound	Fraction of animals showing reactions at specific test intervals		
	24 hr	48 hr	72 hr
PdO	0/6	0/6	0/6
PdCl	6/6	6/6	6/6
PtO	0/6	0/6	0/6
PtCl	0/6	0/6	0/6

REFERENCE

1. Code of Federal Regulations, Title 21, Part 191.12, Rev. April 1, 1973

THE RELATIVE EFFECTS OF PLATINUM AND PALLADIUM ON THE RAT VISUAL EVOKED POTENTIAL

J. P. Lewkowski, T. Hessendarp, W. Moore, and J. F. Stara

The rat visual evoked potential is being utilized as a screening technique to determine the relative short-term effects of various toxic agents on general central nervous system function. More than ninety anesthetized rats have been exposed to metals including platinum and palladium via intravenous injection in the past year. The resulting changes in the rat visual evoked potential have been analyzed using various methods including computer averaging techniques.

The results have indicated that this screening technique may be important in assessing the significant acute effects of various pollutants on central nervous system function under these experimental conditions. Table 1 indicates the threshold dose of the particular metal that elicited a reproducible change in the visual evoked potential in at least 50 percent of the rats studied. The typical effect observed within the first five minutes after injection is also noted.

TABLE 1

Cation	Threshold Response of Approximately 50%(mg/kg)	Number Responding / Total Tested	Typical Effect Observed
Co	0.010	6/9	Increased late (180-500msec.)Negativity (3) Entire amplitude decreased(3)
Cd	0.50	7/13	Increased initial (40-50 msec.) and late negativity
Cr	0.70	10/15	Increased late negativity
Pd	1.0	11/20	Increased initial and late negativity
Mn	2.0	13/18	Increased initial and late negativity
Ba	2.0	6/10	Change in late portion of the evoked potential usually an increased negativity but a decreased negativity was also periodically observed.
Pt	<10.0	0/6	Little effect

Therefore, the relative short-term effect of the intravenous administration of these metals on the rat visual evoked potential may be ranked as follows:

Co > Cd, Cr, Pd > Ba, Mn > Pt

As a result, if a similar blood level of palladium and platinum is assumed, it would appear that palladium has a greater effect on general central nervous system function under the experimental conditions of this particular screening technique. It should be noted that these observed changes may not be due to a direct effect on the central nervous system. Further experimentation is currently underway to determine whether these effects are direct or due to indirect factors which are the result of other physiological changes. In addition, more quantitative and less subjective methods for determining these thresholds are currently being utilized in an attempt to more precisely determine the relative central nervous sytem toxicity of these metals.

A PRELIMINARY REPORT ON THE CARDIOVASCULAR ACTIONS OF PALLADIUM

M. J. Wiester

INTRODUCTION

Palladium chloride ($PdCl_2$) has been shown by Orestano to be extremely toxic when given intravenously (iv).[1] Rabbits rapidly injected with 0.6 mg/kg quickly died, with damage chiefly to the heart. The nature of the heart damage was not further defined, and there is very little other information in the literature addressing this subject. The purpose of this study is to measure the effects of palladium solutions on heart rate, ECG pattern, blood pressure, cardiac contractility (dp/dt), and breathing for 1 hr following iv injection.

METHODS

Sprague Dawley male rats (300 ± 50 g) were surgically prepared 1 day before use. Surgery consisted of catherization of the abdominal aorta with tubing (#50 P.E.) for measurement of blood pressure; tubing (#10 P.E.) was also inserted into the femoral vein to accomodate iv injections. Both catheters were guided through the subcutaneous tissue to the back region, via a puncture wound through the skin to the outside. Six small silver electrodes, fitted with micro-strip connector pins, were inserted under the skin and sutured. These electrodes were arranged laterally so that four were near the limbs to record the ECG and two were on the lateral surface of the rib cage for respiratory measurements. Following surgery, the rats were returned to their cages and given food and water ad libitum (Purina Lab Chow and tapwater).

For testing, an unanesthetized animal was placed in a plastic tubular holder for the duration of the experiment, and sensor leads were fed to a recorder (Figure 1). The measurement system is diagrammed in Figure 2. After a 30-min stabilization or control period, the Pd solution was injected and washed in with saline. The total volume of the dose and wash solution was 0.75 ml, and total infusion time was 1 min. Effects of the injection were then observed for 60 min. Control animals were injected with 0.75 ml of saline and treated the same.

RESULTS AND COMMENTS

$PdCl_2$ exerted an immediate cardiovascular effect in the unanesthetized rat. The most pronounced effect was seen on the electrical integrity of the heart. A total of 10 animals were dosed in amounts ranging from 1.14 to 5.9 mg $PdCl_2$/kg, and in each instance, premature ventricular contractions (PVC) were noted within 1 min after dose initiation. PVC's were never seen during the 30-min control periods or in control animal experiments (5 rats). Doses between 1.14 to 1.75 mg/kg resulted in mild episodes of PVC's following the injection, with no consequential fall in blood pressure. These arrhythmias continued for 3 to 4 min, then the ECG stablized. This stability was dependent, however, on the quiet state of the animal. If the rat moved or showed signs of distress, PVC's reappeared. Rats that received doses between 1.75 and 5.9 mg/kg experienced gross alterations in the ECG pattern following injection. If the cardiac arrhythmias were intermittent or of such a nature as to allow adequate filling and pumping, then the animal survived (Figure 3). The surviving animals were able to maintain sufficient blood pressure levels during the critical 3- to 4-min period following injection.

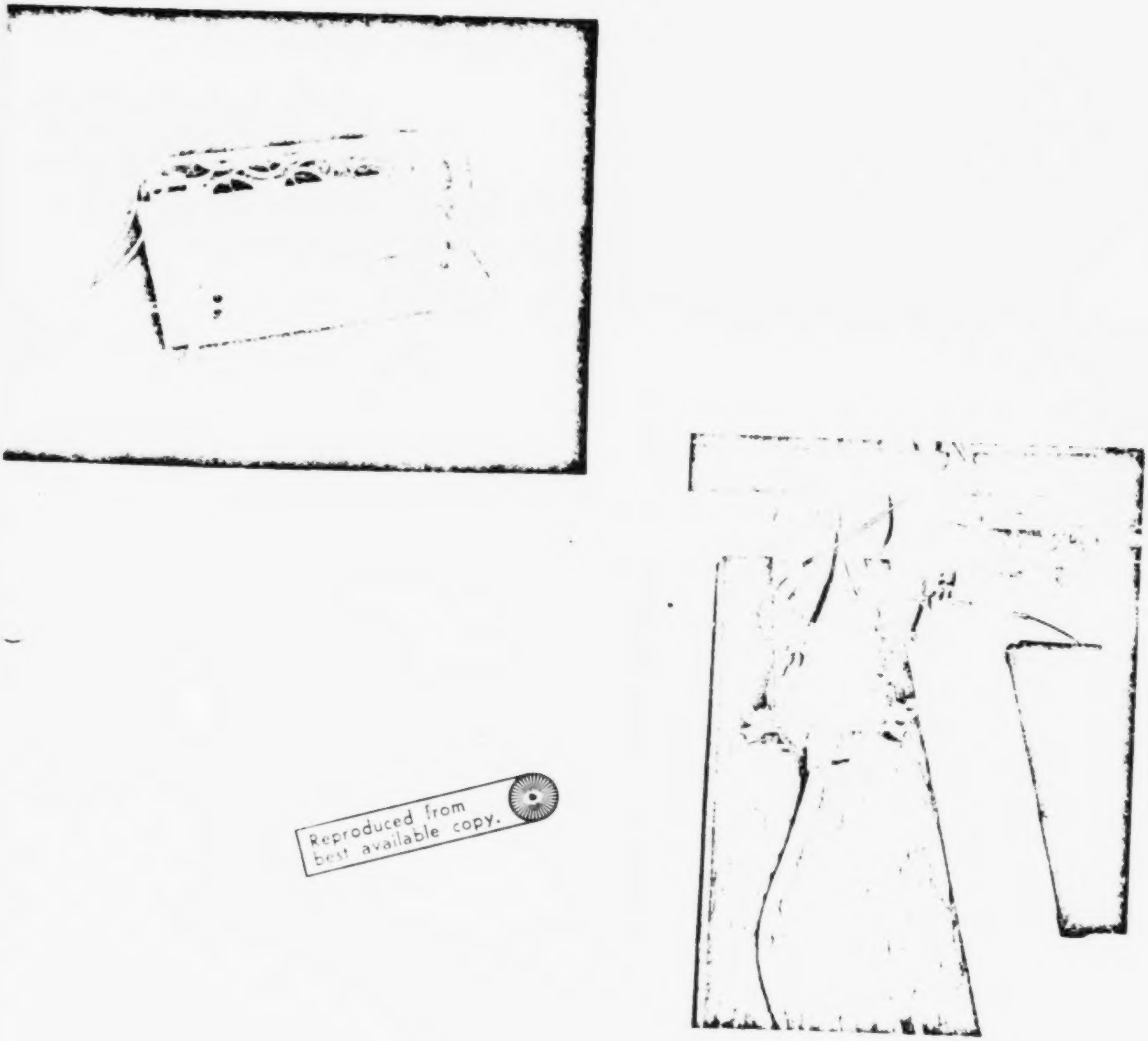

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FIGURE 1. PLASTIC RAT HOLDER.   HOLDER WITH RAT AND POLYGRAPH LEADS

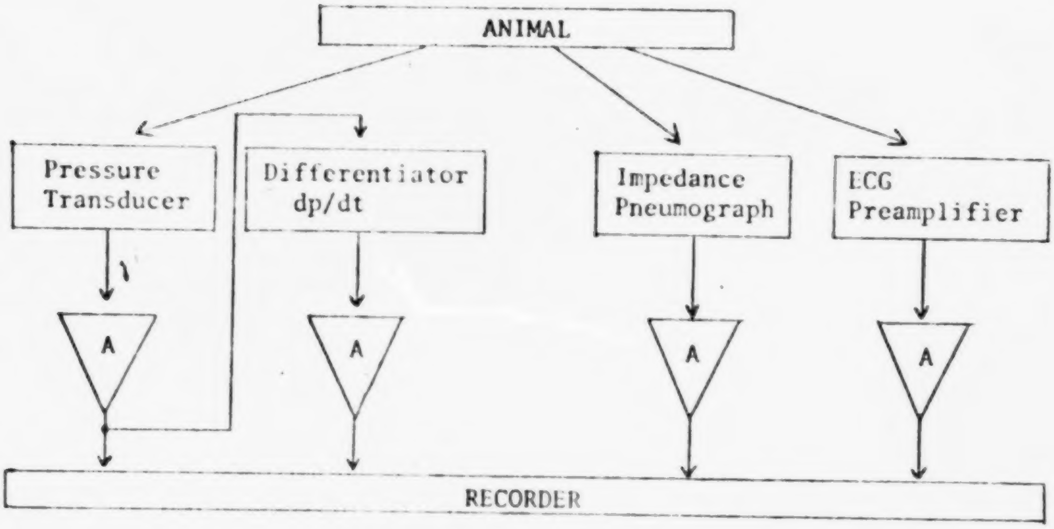

ANIMAL
Pressure Transducer
Differentiator dp/dt
Impedance Pneumograph
ECG Preamplifier
A
A
A
A
RECORDER

Figure 2. Block diagram of recording system.

The pressure transducer is for measurement of arterial blood pressure and is calibrated with a Hg manometer (Miller Instrument).

The differentiator records maximum rate of change of aortic pressure (time contant of 1 msc) calibrated with an osciloscope.

The Impedance pneumograph monotirs rate and relative depth of respiration (Narco Bio-Systems).

The ECG preamplifier (Grass) Lead 2 was recorded.

Polygraph: (Grass 7C)

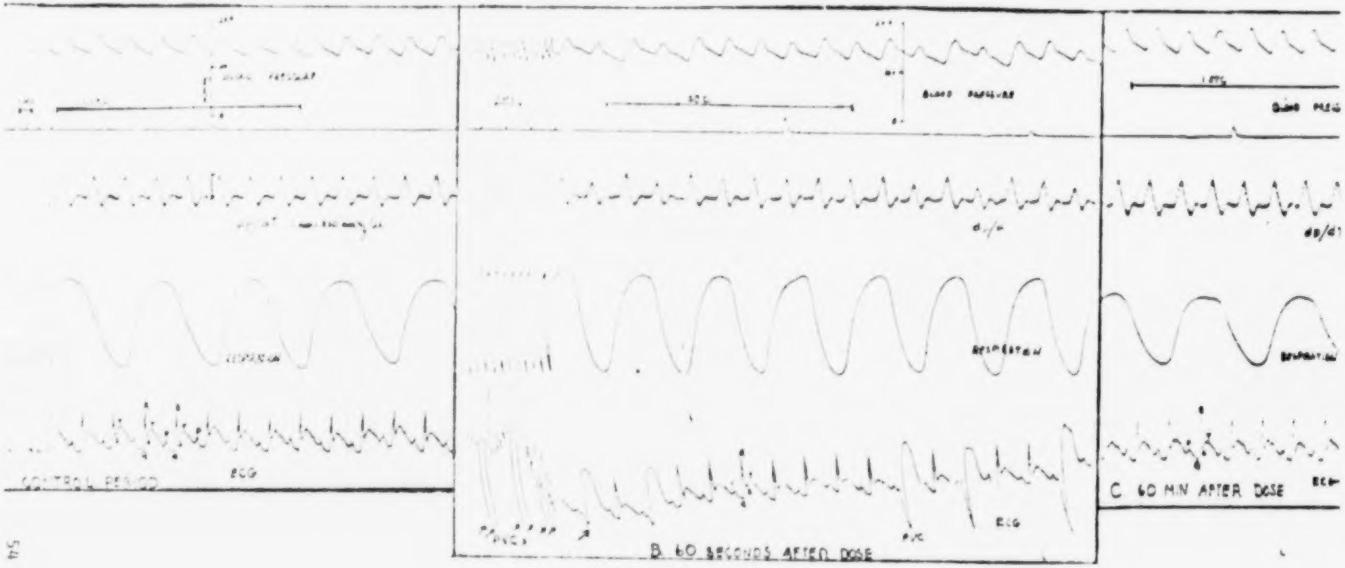


Fig. 3 Rat #4 A. Polygraph recording 25 minutes into the control period. Aortic blood pressure is 165/125. Electronic differentation of the blood pressure signal is displayed as dp/dt. The upward deflection shows maximum rate ofpressure development, which for this pressure pulse is 3,000 mmHg/sec. dp/dt reflects the contractile state of cardia muscle. The respiration record shows the rate and relative depth of breathing. The ECG is derived from lead 2. For this lead a prominant P wave and R wave can be defined. The Q, S, and T waves are somewhat less specific. However, th pattern is dependable and remains unchanged throughout control periods. Heart Rate = 460 beats/min.

B. This section shows the measurements immediately following the I.V. injection of 2.04 mg/kg $PdCl_2$. Gross abnormalit can be seen in the ECG. PVC's are not frequent enough to cause a detrimental fall in blood pressure. Breathing was no altered. Similar irregularities continued for approximately 3 minutes. The animal survived.

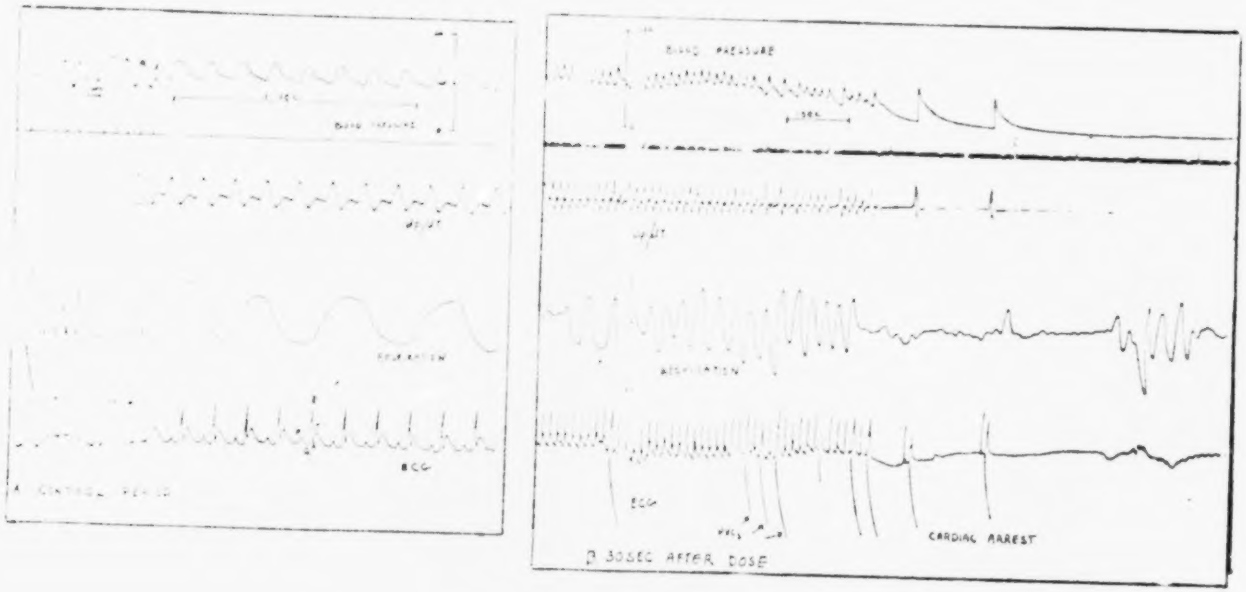
C. One hour following the injection blood pressure had increased to 185/140 mmHg, dp/dt = 3660 mmHg/sec., the ECG show no gross abnormalities, heart rate = 408 beats/min. and breathing was unchanged.

The surviving rats also reestablished a stable ECG during the 1-hr observation period, and like the low-dose animals, they were susceptible to arrhythmias if they became agitated. Rats that succumbed after receiving $PdCl_2$ intravenously suffered gross alterations in the ECG accompanied by a precipitous fall in blood pressure. After the aortic pressure fell, breathing became erratic and the ECG continued to deteriorate (Figure 4). Death usually occurred within 4 min after injection. Additional ECG abnormalities (other than PVC's), that were seen after injection of $PdCl_2$ were extra p waves, large S waves, and various degrees of A-V block.

Rats surviving a $PdCl_2$ injection developed elevated blood pressures that persisted throughout the 1-hr observation period. Systolic pressure increased 20 to 50 mm Hg, and diastolic pressure increased 10 to 20. Heart rates correspondingly decreased, and dp/dt changed very little.

Intravenous $PdCl_2$ appeared to have no initial effect on respiration. Changes in breathing were seen; however, the changes followed gross cardiac arrhythmias and falling blood pressures. If the rat reestablished a steady and productive heartbeat, and thus survived the injection, breathing returned to control values and remained stable.

Palladium sulfate ($PdSO_4$) when given to rats was found to cause cardiovascular and respiratory effects similar to $PdCl_2$. It came to our attention while examining effects of $PdSO_4$ solutions that on aging, solutions became less toxic. To combat this problem, a $PdSO_4$ injection solution was prepared at a pH of 0.5 and analyzed by a atomic absorption throughout the period of use. Since this was not suspected while testing $PdCl_4$, there is some question as to the accuracy of the injected $PdCl_4$ dose.



g. 4 Rat #7 A. Recording 30 minutes into control period - blood pressure = 125/90 mmHg. dp/dt = 3,200 mmHg/sec. art rate = 450 beats/min., ECG normal pattern. Breathing frequency = 132/min. - irregular pattern due to animal movement

. Recording showing gross abnormalities in the ECG, declining blood pressure and death of the animal immediately llowing I.V. injection of 2.75 mg/kg $PdCl_2$.

$PdSO_4$ was administered in doses ranging between 0.5-2 mg Pd^{++}/kg bw. ECG changes, like those described with $PdCl_2$, were observed during the injection period. Initial interruption of the cardiac cycle occurred at 0.5 mg Pd^{++}/kg bw. Animals showed deleterious changes resulting in significant decreases in blood pressure by the time 0.9 mg/kg had been injected. Eleven of 13 rats died during the hour following the dose. One, which received 0.5 mg/kg, experienced only rhythmic irregularities following injection with no sustaining symptoms. The other survivor (1 mg/kg bw) recovered from the cardiac irregularities; however, its systolic blood pressure increased 80 mmHg and diastolic 40 mmHg and persisted throughout the recovery period.

Results from the preliminary experiments described above indicate that $PdCl_2$, or $PdSO_4$, when injected iv, acts as a nonspecific cardiac muscle irritant as well as a peripheral vasoconstrictor. Since the chloride salt strongly dissociates in solution ($PdCl_2 \overset{>}{<} Pd^{++} + 2\ Cl^-$), the Pd ion itself may be the irritant. Effects seen might be due to the release of catecholamines or to stimulation of adrenergic receptors located in the cardiovascular system by the metal ion.

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AUTOMOTIVE EMISSION STUDIES WITH AND WITHOUT CATALYTIC CONVERTERS

AUTO EXHAUST FACILITY MODIFICATION

R. G. Hinners and J. E. Burkart

INTRODUCTION

The auto exhaust generating system has recently been modified at the Environmental Toxicology Research Laboratory. This paper updates several others [1,2] describing the earlier facilities for the production of irradiated and nonirradiated gasoline engine exhaust-air mixtures. In addition, this study is intended as a reference for biologically oriented papers discussing the health effects of auto exhaust.

The toxicity assessment of mobile emissions (TAME) project represents a series of acute and subacute bio-effect studies that test experimental animals exposed to whole automobile-exhaust emissions with fuel additives and/or with or without a catalytic converter. Briefly, the exhaust gases are generated by an engine-dynamometer unit and mixed with clean, conditioned air in a dilution system to produce the desired concentration. The exhaust-gas mixture is divided, with one part flowing directly to animal exposure chambers, and the remainder flowing through irradiation chambers to other animal chambers. The recent changes that have been made in the system include an air-dilution tube for the immediate mixing of the entire raw exhaust emissions with conditioned air, and a large mixing chamber after the dilution tube. This discussion also provides information on air supply, engine cycle, fuel supply, and other minor changes that have been made.

Dilution Tube

The effluent from the engine exhaust system is passed into an air dilution tube through flexible stainless steel tubing connected to the muffler. The dilution tube is 58.4 cm (23 in) in diameter and made from 10 gauge stainless steel plate, rolled and welded. Dilution air enters the tube through a 90° elbow from a remote supply source. Located between the flanges of these two tube sections is a mixing baffle plate with a 18.4 cm (7 1/4-in) diameter hole bored in the center. The incoming dilution air is forced under pressure through this hole to mix with the raw exhaust. The tailpipe exhaust inlet elbow enters 90° to the tube axis and is bent 90° again, so that the flow axis of the exhaust outlet coincides with the center line axis of the dilution tube. The exit end of the 5.08 cm (2-in) diameter stainless steel exhaust elbow is in the same plane as the baffle. Located on top of and outside the dilution tube, at the baffle plate, are two quick-disconnect couplings. One allows the end of the flexible 5.08 cm (2-in) I.D. exhaust pipe from the muffler to connect with the dilution tube, and the other connects to the outside atmosphere. A blank plug is installed in the disconnecting coupling to the dilution tube when the exhaust is vented outdoors. System back pressure at this point is 10.16 cm (4-in) water. This feature provides the capability of varying the modes of engine operation for aerometry and allows interruption of animal exposures.

By operating a damper in the air supply line, the dilution ratio can be controlled. To retain the particulate matter in suspension and prevent condensation, it is necessary to dilute the whole exhaust with at least 8 parts of air to 1 part of exhaust. For each pound of fuel burned, approximately a pound of water is formed, and some condensation occurs if the exhaust is not immediately diluted with dry air. Also to prevent condensation, the outside of the dilution tube is insulated, since engine room temperature often exceeds 90F, and dilution air temperature averages 50F and 67 percent relative humidity. The main portion of the dilution tube consists of two 2.14 m (7-ft) long flanged sections; the tube is then reduced through a transition to a 15.24 cm (6-in) diameter and enters the mixing chamber.

Mixing Chamber

The diluted auto exhaust enters the mixing chamber, formerly used as an irradiation chamber, through a 15.24 cm (6-in) diameter stainless steel pipe opening in the side wall. An elbow discharges the exhaust in front of and parallel with a tube-axial fan, controlled at a low rpm by a Zero Max unit, to mix the entering auto exhaust with the chamber atmosphere.

The chamber is 7.17 m (23 1/2 ft) long, 1.22 m (4 ft) wide, and 2.44 m (8 ft) high, with a volume of 19.34 m^3 (683 ft^3). The sides consist of a framework of aluminum structural members holding metal panels to replace the plastic windows. The aluminum sheet metal panels are clamped and sealed by means of pressure screws and gasketed channels. Previous studies with a reference fuel, to which had been added methylcyclopentadienyl manganese tricarbonyl (MMT) as an antiknock additive, required darkness because of the light sensitivity of the MMT. The top, bottom, and ends of the chamber are formed of .64 cm (1/4-in) thick aluminum plate welded on both sides at all seams to prevent leakage.

At the end of the chamber opposite the entry port is a 15.24 cm (6-in) diameter line with a motorized damper control vented to the atmosphere. Another 15.24 cm (6-in) diameter outlet pipe from the chamber supplies the exhaust either to irradiation chambers or to raw-exhaust animal exposure chambers. A pressure sensor, which is adjustable and located downstream of the chamber exit line, controls the motorized damper in the vent line to maintain 5.08 cm (2-in) of positive water pressure in the chamber.

Irradiation Chambers

The photochemical reactions that result from the exposure of the diluted raw exhaust to artificial sunlight take place in five irradiation chambers. Fluorescent lighting panels composed of blue lamps, black lamps, and sun lamps outside the chamber pass intense ultraviolet radiation through windows of Teflon FEP fluorcarbon film. One irradiation chamber is needed to provide the atmosphere for each animal exposure chamber. Normal flow through the irradiation chambers is .31 m^3/min (11 cfm), which results in 15 air changes per hour in the animal exposure chambers. In some instances, however, the flow has been reduced by one-half the normal, which, of course, doubles the irradiation time. One of the original irradiation chambers used in previous exhaust studies has been converted into a mixing chamber, which is described separately.

At a volume of 19.34 m^3 (683 ft^3) and .31 m^3/min (11 cfm) flow, 43 min is needed to achieve 50 percent of inlet concentration when "building up" from zero. Approximately five times 43 min (3 1/2 hr) are needed to reach equilibrium at the inlet concentration; decay time is also 3 1/2 hr.

Air Supply

The air purifier unit provides, at maximum, 15.6 m^3/min (550 cfm) of chemical, biologically, and radiologically (CBR) filtered and conditioned air. Inside building air is passed through a cooling coil to lower the temperature to 40F (saturated at coil outlet); there is no reheating or humidification. Therefore, if the relative humidity of the outside air drops below 36 grains of moisture per pound of dry air, the relative humidity in the final exposure chamber will also vary. Usually there is no problem maintaining constant relative humidity, but occasionally on very dry days, there is a change.

The humidifier is turned off because of the constant need for cool dry air to mix with hot, wet raw exhaust. Exposure chambers on control air are supplied from a separate CBR filtered source, with controls set to maintain 72 ± 2F and 55 ± 5 percent humidity in the animal chambers. The same air is also ducted to the air filter inlet of the engine being used for the study, since a change in humidity affects the NO_x emissions from the engine.

Engine Cycle

The dynamometer driving schedule for the Chevrolet engines consists of a repetitive series of idle, acceleration, cruise, and deceleration modes of fixed time sequences and rates. Table 1 shows the modified California cycle used in the fuel emission studies.

Table 1. MODIFIED CALIFORNIA CYCLE USED IN THE FUEL EMISSION STUDIES

Mode	Speed, mph	Km/hr	Time, seconds
Idle	0	0	20
Acceleration	0 to 30	0 to 48.27	14
Cruise	30	48.27	15
Deceleration	30 to 15	48.27 to 24.14	11
Cruise	15	24.14	15
Acceleration	15 to 49	24.14 to 78.84	29
Peak	49 to 50	78.84 to 80.45	1.5
Deceleration	50 to 0	80.45 to 0	31.5
Total			137 sec.

Replacement of the California cycle with the LA-4 cycle controller was considered at one time. However, after consultation with other experts in the field, a decision was made to continue with the California cycle because the exhaust is being further diluted to prescribed levels and both cycles are very similar, since they reflect transient as well as cruise operation. The key to this research is comparative toxicity, and either cycle is satisfactory to achieve this goal. A simple, repetitive cycle that is easily controlled over long periods of time (weeks) is of prime importance to toxicologic investigations.

Fuel Selection

The gasoline selected for use in the Chevrolet engines as a standard reference, baseline fuel for evaluation of engine, fuel, and additive variables was the American Oil Company's, Unleaded 91 Octane Test Fuel, Intermediate Grade Indolene Clear. For reference, it was important that the fuel be of precise and reproducible composition and character, free of lead and other additives (except as specifically noted), and similar to high-volume, regular market gasoline. This gasoline has been used for such purposes in research and development by industry and other agencies. The lubrication oil selected was Texaco Havoline 30W, API service specification SE. Table II represents a comparison and product analysis of the two gasoline deliveries used for exhaust emission studies during 1973.

Table 2. COMPARISON AND ANALYSIS OF THE TWO GASOLINE DELIVERIES USED FOR EXHAUST EMISSION STUDIES IN 1973*

Property	Shipment No.	
	*1	2
Date delivered	3/30/73	10/29/73
Quantity, gal	2,000	1,500
Octane No., research	91.4	91.3
Octane No., motor	82.9	82.5
Lead Atm. Abs., g/gal	0.01	0.01
Phosphorus, g/gal.	0.002	0.00
Sulfur, wt. %	0.04	0.04
Aromatics, vol %	25.4	23.5
Olefins, vol %	11.8	9.9
Gum, existent, mg/100 cc	0.8	1.0
Gravity, OAPI	61.4	61.5
Oxidation stability, min.	600+	600+
Reid vapor pressure, lbs.	9.1	9.0

*Shipment No. 1 was used for studies G, H, I, and J. Shipment No. 2 was used for study K with Thiophene added to produce 0.10 percent by weight sulfur.

Fuel Storage and Handling

Local fire and safety regulations require flammable liquids to be stored outside the building, so two underground fuel storage tanks were installed on the property near a blacktop driveway. To promote chemical stability of the fuel during storage, the tanks are maintained under slight positive pressure, with nitrogen supplied from cylinders and controlled by a pressure regulator. A double-acting pressure- and vacuum-relief valve on the vent outlet compensates for changes that result from fuel being pumped out or temperature increasing, which would alter the pressure of the nitrogen gas cover. Each tank is of 7571 l (2,000-gal) capacity and equipped with an electric fuel pump rated at 56.8 l (15gal) per min.

Outside the building wall and next to the engine room is a 68.1 l (18-gal) marine fuel tank sitting on a weight scale and connected to a remote electric fuel gauge located in the instrument panel. Transportation of the test fuel from the main underground storage supply to the 1 day supply tank is effected by a mobile safety dispenser cart made especially for transporting flammable liquids. The 227 l (60-gal) capacity cart carries the Underwriters Laboratories' approval as a portable flammable liquid tank and is equipped with transfer pump and grounding reel. The cart also has a drain, and removing the pump gives access to a 10.2 cm (4-in) handhole for reaching and cleaning the tank interior between fuel changes. Similarly, the 68.1 l (18-gal) marine tank can easily be inverted for cleaning when required.

An alteration in the composition of the reference fuel for a study is made by the addition of the required amount of chemical to a full cart batch. Thus studies requiring the testing of fuel additives such as MMT or thiophene to increase the sulfur content can be conducted by mixing only the amount of fuel necessary.

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ENGINES AND OPERATING CONDITIONS FOR CATALYTIC EMISSION STUDIES

R. G. Hinners and J. K. Burkart

During 1973, animal exposure studies were conducted in the Environmental Toxicology Research Laboratory (ETRL), National Environmental Research Center (NERC), Cincinnati, Ohio, to assess the relative health hazard of automobile exhaust emitted from engines with and without catalytic converters, using similar engine settings. Automotive exhaust catalysts were developed to lower exhaust emissions of the three pollutants specifically listed in the Federal Clean Air Act of 1970: carbon monoxide, hydrocarbons (by oxidation), and oxides of nitrogen (by reduction). Three possible conditions could result in other emissions:

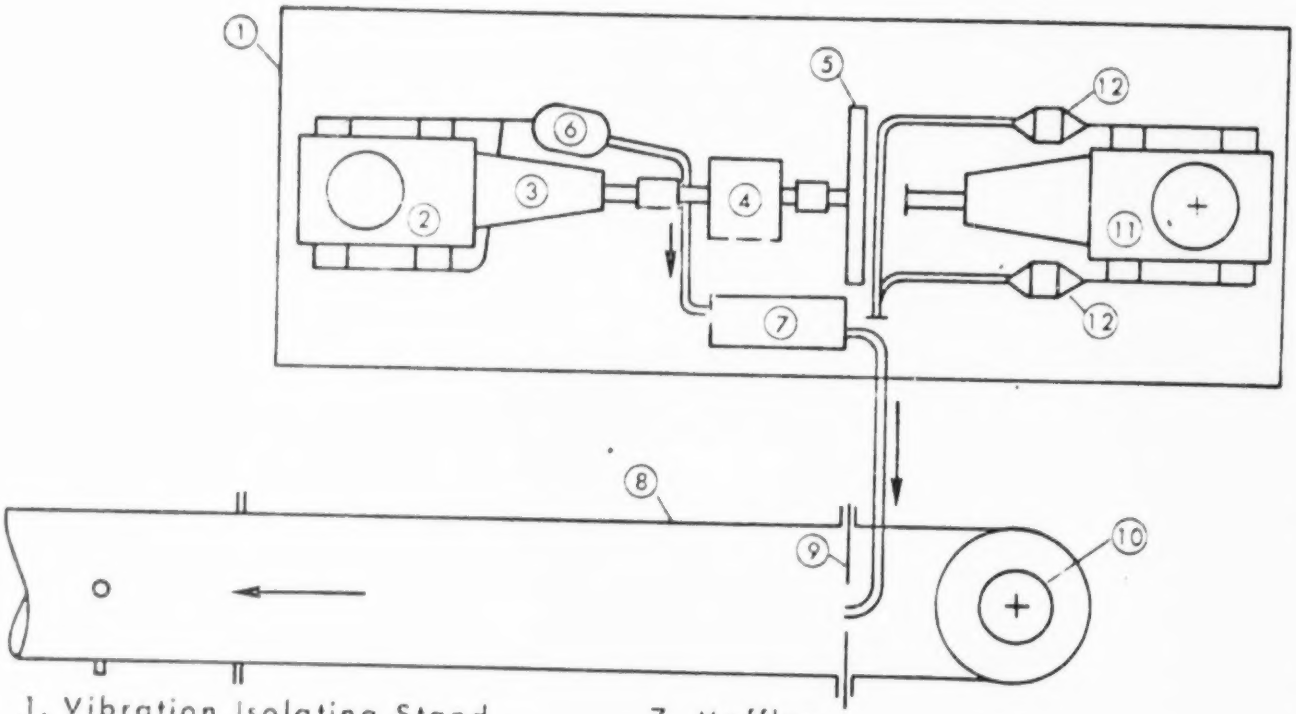
1. As the hot catalyts promote the oxidation of carbon monoxide and hydrocarbons in automotive exhaust, converting them to carbon dioxide and water, they may simultaneously convert the organic sulfur compounds present in all gasoline to sulfuric acid mist and eventually to sulfates.
2. The metals used in the converter, such as platinum and palladium, may be emitted under conditions of catalyst degradation from the exhaust pipe in fine particles and be suspended in the air.
3. The total emissions may be altered and may produce different quantities or new species.

In order to perform the assigned tasks, this laboratory recently acquired and installed two new engines equipped with catalytic converters from the General Motors Company and the Ford Motor Company. The General Motors engine (350 CID) is a 1973 production engine and has the following controls: (1) exhaust gas recirculation, (2) an air pump, and (3) one catalytic converter (pelletized type, noble metal oxidation catalyst). (Catalyst by Engelhard Co.)

The Ford engine (400 CID) is a 1975 prototype, R-6 engine with R-14 calibration and the following controls: (1) exhaust gas recirculation, (2) an air pump, (3) a fluidic spark delay valve, (4) various temperature sensing triggers, and (5) catalytic converters of the monolith, noble metal oxidation type (two converters of this type are required, one for each bank of cylinders). (Catalyst by Matthey-Bishop Co.) A schematic view of the double engine-dynamometer unit and dilution tube is presented in Figure 1.

During the toxicity assessment of mobile emissions (TAME) (studies H, I, J, and K), the 1973 Chevrolet engine was operated continuously for 7 days using the California cycle. Comprehensive data for comparison of study-engine operating conditions is given in Table 1.

TAME K was designed to test emissions and bioeffects of a high-sulfur gasoline free of other undesirable substances such as lead. Thiophene was added to produce a sulfur content of 1,000 ppm in the control fuel, Indolene. Sulfur compounds present in gasoline are mainly in the form of polysulfides and thiophene compounds with an insignificant amount of hydrogen sulfide.



1. Vibration Isolating Stand
2. 1973 Chev. V-8 350 C.I.D.
3. Turbohydromatic Transmission
4. Dynamometer Absorption Unit
5. Flywheel
6. Catalytic Converter
7. Muffler
8. Dilution Tube
9. Baffle Plate
10. Dilution Air Supply
11. 1975 Ford V-8 400 C.I.D.
12. Catalytic Converters

Figure 1. Schematic view of the double engine-dynamometer unit and dilution tube.

Table 1. COMPARISON OF STUDY-ENGINE OPERATING CONDITIONS

Item	TAME H	TAME I	TAME J	TAME K
Dates	9/10 - 17	10/10 - 17	10/24 - 31	11/14 - 21
Fuel	Ref. only	Ref. only	Ref. only	Ref. + sulfur
Engine	'73 Chev., w/catalyst	'73 Chev., no catalyst	'73 Chev., w/catalyst	'73 Chev., w/catalyst
Engine hours	62-230	255-425	444-615	675-841
Study hours	168	170	171	166
Engine miles	4,600	8,500	12,300	16,820
Cumulative catalyst hours	244	244	465	632
Catalyst miles	4,880	4,880	9,300	12,640
Total fuel (lb)	1,533	1,545	1,601	1,495
Fuel, lb/hr	9.10	9.08	9.40	9.02
Exhaust Oxygen (%)	4.9	N.A.	4.2	4.7
Air/fuel ratio	-	14.4 cycling 12.4 idle	-	-
Oil consumption (qt)	1-1/8	1/2	1/4	1/4
Dilution ratio	8.0/1	9.6/1	8.7/1	9.5/1
Dilution air flow (average SCFM)	318	305	310	324
Dilution tube temperature (average °F)	106	101	114	101

Our testing procedures reported and confirmed that the addition of oxidation catalysts to the automotive exhaust system causes an increase in the emitted particulate material (consisting mainly of hydrated sulfuric acid droplets) as a result of the oxidation of organic sulfur compounds in gasoline. Recent national averages of the sulfur content are between 210 and 260 ppm for premium gasoline, and between 390 and 4[illegible]0 ppm for regular gasoline. The Indolene motor fuel used at the ETRL facility had a sulfur content of 0.04 percent by weight, or 440 ppm.

DESIGN AND SYSTEM PERFORMANCE FOR STUDIES OF CATALYTIC EMISSIONS

J. Burkart and R. Hinners

The engine used in these studies was a 1973 Chevrolet 350 C.I.D. production model with EGR, air pump and turbo hydromatic transmission coupled to an "eddy current" absorption dynamometer. The beaded noble metal oxidation catalyst HN-2242 coating was by Engelhard Mineral and Chemical Company.* New road-load data supplied by the EPA Motor Vehicle Emissions Lab were used; they are equivalent to an increase of inertial weight from 1542 kg (3,400 lb) (used on a 1972 Chevrolet) to 1814 kg (4,000 lb). No attempt was made to adjust idle mixture, as in earlier Toxicity Assessment of Mobile Emissions (TAME) studies A through G, and carburetor limiters remained in place. In TAME H, the engine was run as-received, except for setting idle speed, dwell, and timing. Maintenance performed before TAME I, J, and K consisted of changing the oil and filter, installing new points, condenser, and spark plugs, and setting hot idle speed, dwell, and timing. In addition, before TAME K, new spark plug wires were installed.

For each of the continuous 1-week TAME studies H through K, approximately 5470 km (3,400 miles) were accumulated on the California cycle. Separate cumulative engine miles and catalyst miles are reported, since the catalyst was removed in TAME I, and additional steady-speed runs (without animal exposures) were made to characterize emissions. The dilution ratio is determined by the ratio of average tailpipe CO_2 to dilute CO_2.

Because the variability of tailpipe CO_2 throughout the cycle is small, the problem of obtaining a proportional sample is negligible. Samples for CO_2 detection flow at a constant 1 liter per min through a refrigerated cooler, dessicant dryer, and paper filter to the Beckman Infra Red Model 315. This instrument is calibrated for 15 percent CO_2 full scale and zeroed on dilution air; however, because of the cooler, some small CO_2 loss in the condensate was unavoidable.

For all studies, a continuous trace at constant sample flow on two Mosley (2-pen) recorders was made of tailpipe CO, dilute CO, tailpipe THC, and tailpipe CO_2. The recordings, along with spot checks of tailpipe oxygen and dilute CO_2, monitored engine and dilution system operation.

The TAME schematic in Figure 1 shows sampling points throughout the system, starting with the engine, the catalytic converter, and the standard muffler. The numbers will be referred to for aerometry sample identification except when exposure chambers are sampled; the chamber number and treatment (irradiated, nonirradiated, and clean air) are used.

Some average total particulate losses on a percentage basis are also shown in Figure 1, starting with 100% at point 5 in the dilution tube which was located 2.74m (9 ft.) from the raw exhaust inlet. An overall loss of 39% occurs, with the largest loss (22%) happening between points 5 and 6,2.135m (7 ft) away. The initial decrease due to the gravitational loss of larger particles was anticipated. The reduction in duct size from 58.42cm (23 in.) to 15.24cm (6 in.) diameter was also a factor in particulate loss.

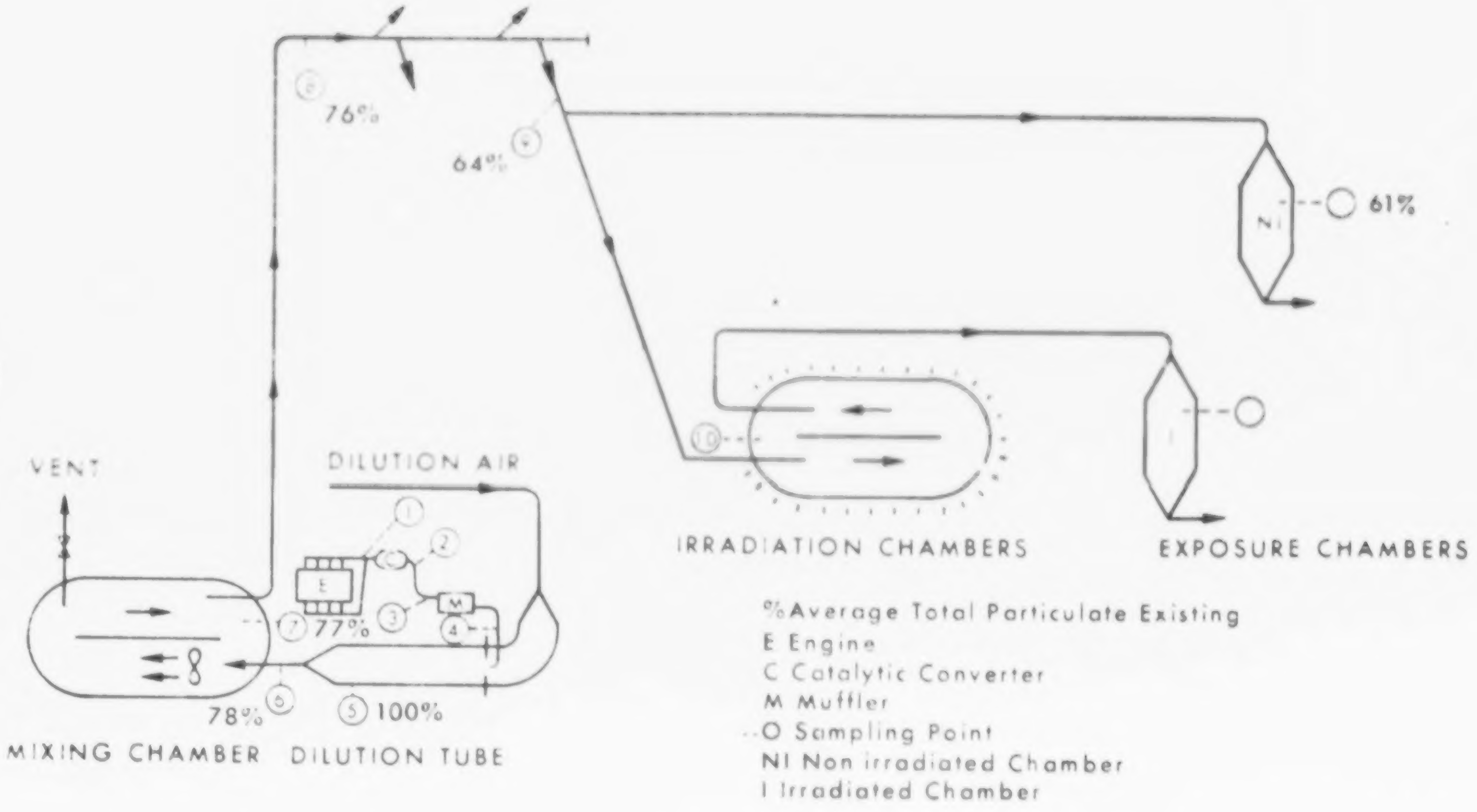

VENT
DILUTION AIR
MIXING CHAMBER
DILUTION TUBE
IRRADIATION CHAMBERS
EXPOSURE CHAMBERS
E
M
NI
I
① ② ③ ④
⑤ 100%
⑥ 78%
⑦ 77%
⑧ 76%
⑨ 64%
⑩
61%
%Average Total Particulate Existing
E Engine
C Catalytic Converter
M Muffler
--O Sampling Point
NI Non irradiated Chamber
I Irradiated Chamber

Figure 1. TAME schematic showing sampling points.

The size of the particulates sampled in the exposure chamber, given as MMED (mass median equivalent diameter), varied between 0.13 and 0.40 micron, with an average of 0.29 micron. The particulate MMED in the dilution tube averaged 1-1/2 to 2 times larger.

The particulate characterization runs were made before the catalyst studies and during a 2-month study on a Mn fuel additive (CI-2) in Indolene. For these runs a 1972 Chevrolet 350 C.I.D. was operated on the "California" cycle and data collected at the midpoint of the study, after the system had been conditioned. Losses vary as the character of the aerosol changes and a different size distribution occurs from changes in engine speed and load. This results in a different particulate loss distribution. A change to high engine speed after a period of lower engine speed operation shows an initial large loss of particulate, due to the gravitational losses of more large particles. The same effect is noted when much cooler dilution air is mixed with the hot exhaust. These observations serve to indicate the variable nature of aerosols. After this study, during the installation of the new engine-catalyst package, the entire system was thoroughly cleaned.

During catalyst studies, the entire tailpipe volume was mixed with the quantities of air given in Figure 2; the resulting dilution tube temperatures are also shown. The dilution air temperature for all studies ranged from 48° to 55°F. Figure 3 depicts tailpipe conditions which include exhaust oxygen content and average catalyst temperature measured at center line of the tailpipe 2.5 cm [1 in] from catalyst outlet. At the tailpipe, the 7-day trend during the catalyst studies (H, J, K) was oxygen decrease, CO_2 increase, and catalyst temperature increase.

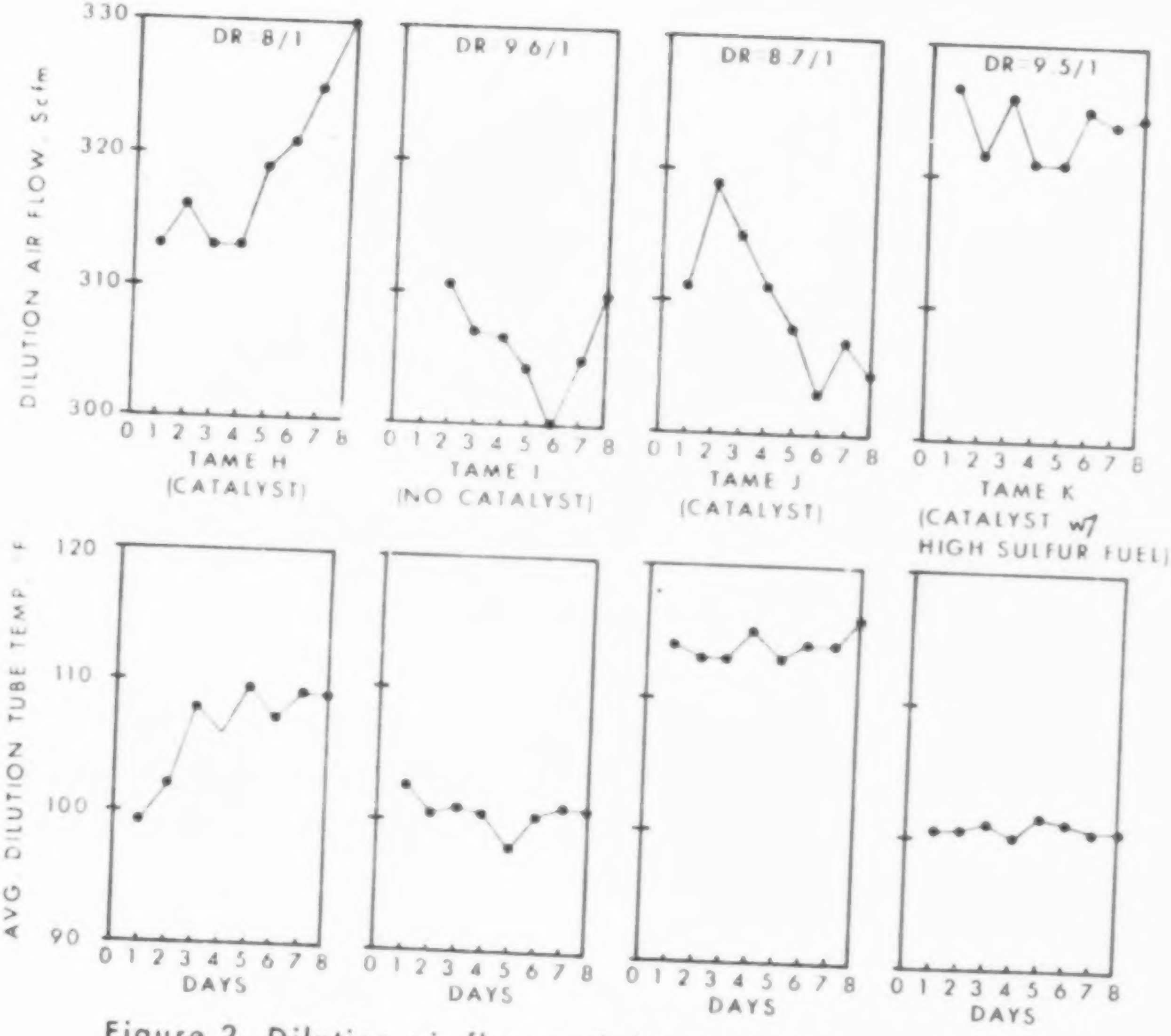


Figure 2. Dilution air flow and dilution tube temperature.

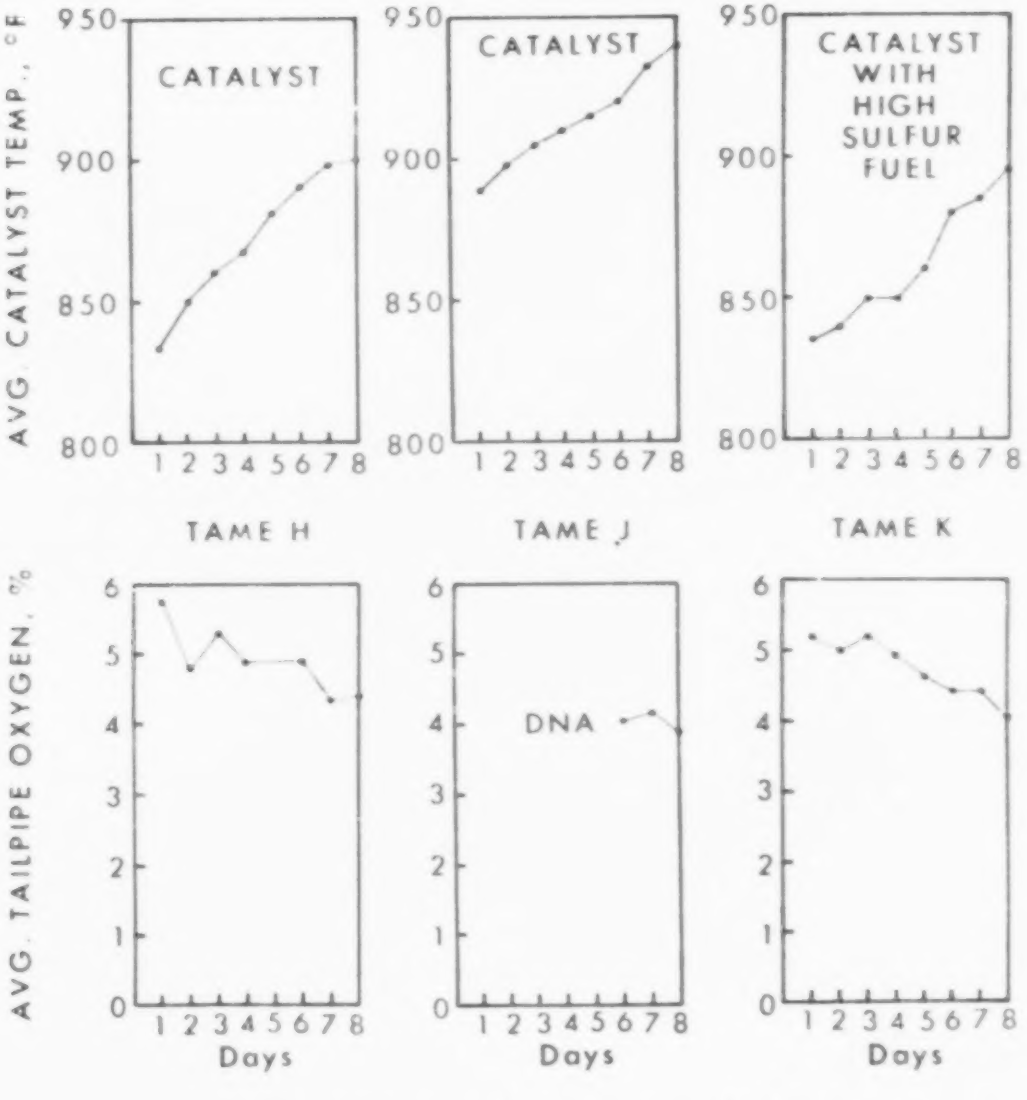


Figure 3. Tailpipe conditions.

Table I shows the General Motors catalyst efficiency when TAME I (without catalyst) average emissions are used as the basis for comparison. Note that the catalyst is more efficient in terms of CO than of HC under the hot cycling condition.

Some initial loss of efficiency may be due to the higher oil consumption during TAME H; also, by the end of that study, No. 3 plug had fouled.

Table 1. GENERAL MOTORS CATALYTIC CONVERTER EFFICIENCY

Item	H	I	J	K
	Average tailpipe concentration (ppm)*			
Carbon monoxide	49	4,739	354	340
Hydrocarbons (as methane)	84	946	169	153
	Total percent reduction below TAME I			
Carbon monoxide	99	--	93	93
Hydrocarbons (as methane)	91	--	82	84

*Calculated from dilute concentrations multipled by dilution ratio minus one.

Basic specifications for the 1973 Chevrolet engine are shown below in Table 2.

Table 2. Chevrolet Engine System

	1973
Displacement	350 C.I.D.
Compression Ratio	8.5/1
Carburetor Type	Roch. 2GV 1-1/2 (#7043114)
Distributor	# 1112168
Mech. Adv. Unit	C 4815
Vacuum Adv. Unit	C6020(46914)
Dwell	30°
Initial Timing	8°BTC
Maximum Vacuum Advance	14°
Emission Control Equipment:	Air pump Rich tune (A/F 14.5/1) Timed port Vac. Adv. EGR 11633 (LF 7040437)

Data for exposure chamber temperature and relative humidity are presented in Figure 4. The temperature profiles appear favorable, however, the relative humidity for chambers receiving exhaust were consistently above 60 per cent relative humidity while the reverse was true for control air chambers.

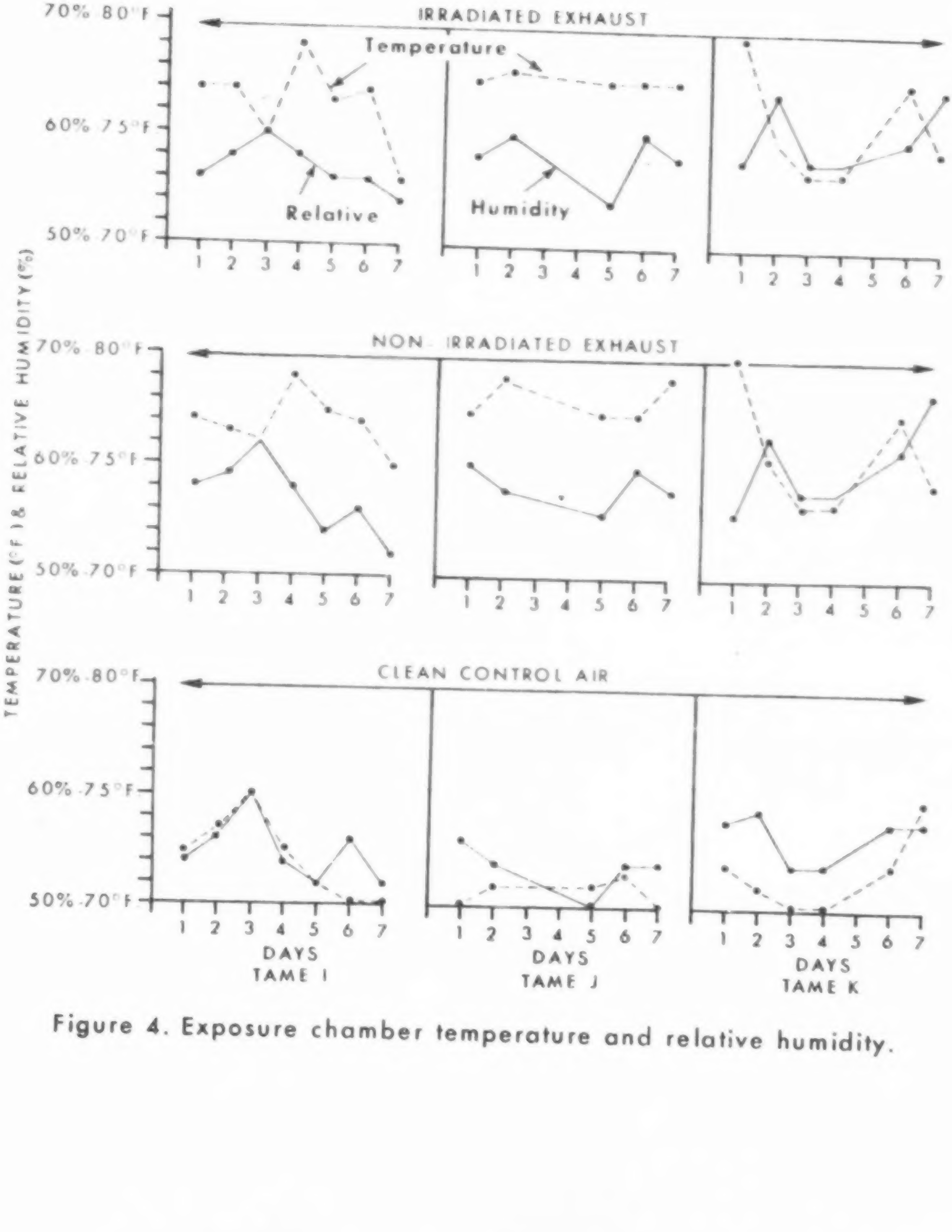


Figure 4. Exposure chamber temperature and relative humidity.

EXHAUST EMISSIONS DURING STEADY SPEED RUNS WITH THE CATALYTIC CONVERTER IN THE EXHAUST SYSTEM

M. Malanchuk, N. Barkley, G. Contner
M. Richards, and R. Slater

INTRODUCTION

In preparation for studies on the exposure of animals to the exhaust emissions from catalytic-equipped systems preliminary runs were made with the 350 CID Chevrolet engine operating at constant speeds. Information was sought that would indicate the levels of constitutents different from those of previous runs made under different engine operating conditions. The data were needed particularly with reference to sulfur compounds and acidity of the emissions. Preparations were made to test for sulfates, sulfur dioxide, sulfuric acid, and nitrate components. Sample procedures were adapted by making those changes necessary for quantitative results.

EXPERIMENTAL PROCEDURE

The main effort was directed toward the sampling of particulate matter to establish the nature of the anticipated changed character of the particulate.

Since membrane-type filters used to collect aerosol from the catalytic converter system deteriorated from the corrosive action of the sample, quartz fiber material was used and found favorable for such samplings. Not only did that material resist breakdown, it also did not cause any changes in the nature of the aqueous extraction medium (e.g. pH) after standing as long as 20 to 30 hr.

The sample filters were handled in two different ways. Every filter was weighed immediately after sampling. Some were permitted to stand overnight to equilibrate in the room atmosphere (70-75F, 40-60 percent relative humidity) until the weight had stabilized. Because of the large differences in initial and final weights of many of the samples, the initial values were used to calculate the particulate concentrations in the sampled atmospheres since those values were considered to be more immediately representative of the existing chamber conditions. Other filters, immediately after they were weighed following the sampling, were placed in a measured volume of distilled, deionized water. Conductance and pH measurements were then made to determine ion concentrations--mainly, the acidity of dissolved samples. The aqueous extracts were also used for analysis of particular ion radicals like the sulfate and nitrate groups.

Analytical procedures included the barium chloranilate method[1] and nephelometry for sulfate, the phenol-hypochlorite reaction[2] and ion-specific electrode for ammonia and ammonium compounds, and the hydrazine reaction[3] for nitrate.

Bubblers containing distilled water or a weak acid solution were used to scrub sampled atmospheres for nitrate--and for ammonium-producing components. A sampling train of bubblers similar to that used in stack sampling[1] was arranged for separation of SO_2 from SO_3 in atmospheres drawn from the exhaust pipe before and after the catalytic converter and from the animal exposure chambers. The first bubbler in the train, containing isopropanol, collected SO_3. The succeeding two bubblers, containing hydrogen peroxide, collected the SO_2 and converted it to the sulfate form. In some cases, the follow-up bubblers contained tetrachlormercurate instead of peroxide to trap the SO_2 for analysis by the West-Gaeke method.[4]

None of the animal exposure chambers from which the atmosphere was sampled contained any animals. These chambers previously were hosed down thoroughly with hot water to minimize, if not eliminate, sources of contaminating deposits.

RESULTS

The effects of different engine speeds and of different concentrations of sulfur in the fuel are seen in the concentration values of exhaust emission components in Table 1.

Values of gaseous components are listed first - carbon monoxide (CO), total hydrocarbons as methane (THC), nitrogen oxides (NO_x), with a breakdown into nitric oxide (NO) and nitrogen dioxide (NO_2), the aliphatic hydrocarbons of the C_4-C_5 group examined, olefins of the C_2-C_4 group, and acetylene. Values for particulate material are listed as total particulate and as the sulfate and nitrate concentrations in that particulate.

The first 5 columns of concentration values were obtained from the operation of the engine with the base fuel, Indolene gasoline, and the use of the catalytic converter unit in the immediate exhaust system. The last 4 columns show the concentrations obtained when the Indolene gas was "spiked" with an organic sulfur compound to double the concentration of sulfur in the fuel; in one case, the catalytic converter unit was retained in the exhaust system; in the second case, the unit was removed before the run was started.

TABLE 2. [illegible] EXHAUST EMISSIONS, STEADY SPEED RUNS

Emissions		Regular Indolene gasoline with catalytic converter					High-sulfur Indolene with catalytic converter		High-sulfur Indolene without catalytic converter	
		15 mph	30 mph		50 mph		15 mph		15 mph	
Exhaust Dilution Ratio		7.5/1	6.2/1	(7.5/1)	4.9/1	(7.5/1)	8.1/1	(7.5/1)	8.0/1	(7.5/1)
CO, ppm:	N-I	7	8	(7)	10	(7)	7	(8)	491	(522)
	I	7	8	(7)	10	(7)	7	(8)	-	-
THC, ppm:	N-I	9	9	(8)	4	(3)	8	(9)	93	(99)
	I	8	9	(8)	4	(3)	8	(9)	-	-
NO$_x$, ppm:	N-I	20.0	28.4	(23.5)	102.0	(66.6)	-	-	21.1	(22.5)
	I	19.4	31.8	(26.3)	104.8	(68.5)	-	-	20.3	(21.6)
NO, ppm:	N-I	14.7	21.2	(17.5)	71.9	(46.9)	-	-	13.3	(14.2)
	I	13.2	21.8	(18.0)	63.6	(41.6)	-	-	9.6	(10.2)
NO$_2$, ppm:	N-I	5.3	7.2	(6.0)	30.1	(19.7)	-	-	7.6	(8.3)
	I	6.2	10.0	(8.3)	41.2	(26.9)	-	-	10.7	(11.4)
Aliphatics, ppm:	N-I	0.107	0.113	(0.093)	0.031	(0.020)	0.109	(0.118)	-	-
	I	0.108	0.113	(0.093)	0.026	(0.017)	0.115	(0.124)	-	-
Olefins, ppm:	N-I	0.450	0.465	(0.385)	0.204	(0.133)	0.433	(0.467)	-	-
	I	0.426	0.456	(0.377)	0.195	(0.127)	0.447	(0.483)	-	-
Acetylene, ppm:	N-I	0.025	0.018	(0.015)	0.012	(0.008)	0.018	(0.020)	-	-
	I	0.025	0.020	(0.017)	-	-	0.028	(0.030)	-	-
Particulate, mg/m^3-diluted exhaust		7.20	20.1	(16.6)	20.7	(13.5)	23.7	(25.6)	2.5	(2.67)
	N-I	9.60	22.2	(18.4)	49.3	(32.2)	28.0	(30.2)	3.0	(3.20)
	I	5.20	17.1	(14.1)	44.8	(29.3)	21.4	(23.1)	2.5	(2.67)
Sulfate, mg/m^3-diluted exhaust		4.33	6.18	(5.11)	6.93	(4.53)	13.16	(14.20)	0.54	(0.58)
	N-I	4.80	5.00	(4.14)	4.90	(3.20)	11.86	(12.80)	0.49	(0.52)
	I	3.01	3.94	(3.26)	2.72	(1.78)	10.65	(11.50)	0.49	(0.52)
Nitrate, mg/m^3-diluted exhaust		0.32	-	-	0.47	(0.31)	0.36	(0.39)	0.28	(0.30)
	N-I	0.01	-	-	0.00	(0.00)	0.01	(0.01)	0.04	(0.04)
	I	0.01	-	-	0.31	(0.20)	0.01	(0.01)	0.17	(0.18)

N-I Non-irradiated atmosphere, exposure chamber with
I = Irradiated atmosphere, exposure chamber with

The samples were mainly collected from the animal exposure chambers receiving the diluted exhaust emissions that had been exposed to the irradiation lights (I), and those chambers receiving diluted emissions not treated to the irradiation effects (NI). The particulate samples identified as diluted exhaust were collected from the exhaust system in the immediate range of the engine.

To relate the values from the higher engine speeds and the runs with higher gasoline sulfur to the basic 24 km/hr (15 mph) with its 7.5/1 dilution, the actual values of those runs have been adjusted to equivalent values for a 7.5/1 dilution which are given in brackets.

Since the data apply only to single runs at each of the five different sets of conditions (except the basic 24 km/hr (15 mph) with regular Indolene fuel, where there were two runs for which the average values were calculated), the information must be considered as tentative. Duplicate runs will be made to establish reproducibility and to confirm the results presented.

Nevertheless, large differences in the results between runs were seen, which may be acceptable for what they indicate. The large increase in the nitrogen oxides at the highest speed of 80 km/hr (50 mph) was to be expected (see columns 1-5 of Table 1). There was a concomitant decrease in hydrocarbons. Particulate levels beyond the converter increased with increasing engine speed. Apparently, particulate sulfate concentrations remained the same at different speeds; however, they seem to make up most of the solute of the particulate. Nitrate was present at much lower concentrations.

With the high sulfur (2 x) Indolene gas as fuel, the carbon monoxide and hydrocarbons (total and individual) levels remained the same (columns 6 and 7). The big difference was seen in the total particulate and sulfate contents (about three to four times as much as for the regular Indolene gas).

The engine operating with the high-sulfur fuel but without the catalytic converter had, as expected, much higher levels of carbon monoxide and hydrocarbons. The nitrogen oxide levels were at similar concentrations as those for the 24 km/hr (15 mph) with regular Indolene fuel. The particulate levels (columns 8 and 9) were only about one-tenth of those for the catalytic converter (columns 6 and 7). Sulfate in the particulate was almost negligible by comparison.

Acidity measurements of the particulate from the catalytic-equipped systems were without exception, high enough to allow for all the sulfate to be considered present as sulfuric acid. That is to say that the hydrogen ion concentration as ($2H^+$), measured with a pH meter, was greater than the sulfate ($SO_4^=$) concentration--sometimes by a factor of three. Such high acidity was found unaccountable on the basis of the anionic components measured and the total particulate determined; additional study is needed to resolve the phenomenon. An indication of relative acidity levels with different operating conditions is shown in Table 2. The particulate (columns 8 and 9 of Table 1) in the system without a catalytic converter was, on the other hand, almost completely neutral as measured by a pH meter on its aqueous extract.

Measurements of sulfur components (SO_x) in the undiluted exhaust before and after the catalytic converter showed a 50- to 90-percent decrease of sulfur. That is to say, there was a considerable hold-up of sulfate in the catalyst bed itself.

Table 2. RELATIVE ACIDITY LEVELS OF EXHAUST EMISSION PARTICULATE AT 24 km/hr (15 mph)

Operating Condition	No catalytic converter high-sulfur Indolene fuel	With catalytic converter	
		regular Indolene	high-sulfur Indolene
Relative acidity of particulate	1	65	260
Total particulate @ 7.5/1 dilution mg/m^3	2.7	7.2	25.6

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EFFECT OF CATALYST AND OF FUEL SULFUR CONTENT UPON AUTO EXHAUST EMISSIONS

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R. Slater, J. Burkart, and Y. Yang

INTRODUCTION

Some early studies in the automobile industry have indicated that oxidation-type catalysts in auto exhaust systems generated high levels of sulfuric acid aerosol, as much as 0.1 g of the acid per vehicle mile. It was hypothesized that the engine combustion process converted organic sulfur compounds in the gasoline into sulfur dioxide, and that the dioxide was oxidized by the catalyst to sulfur trioxide, which reacted with water vaper in the exhaust to produce sulfuric acid droplets.

Therefore, cycling speed-runs (as opposed to constant-engine speed-runs) were used for the animal exposure studies, since they more nearly simulate automobile operation in the streets. Measurements of exhaust-emission components were made to determine the levels to which the animals in the studies were exposed. The effective changes in exhaust composition were determined when the catalytic converter unit was added to the exhaust system, and when high-sulfur fuel (0.10 percent sulfur) was substituted for the reference Indolene gasoline (0.05 percent S).

Emission components present in relatively high concentrations were monitored in much the same way as in previous runs.

SAMPLING AND ANALYTICAL PROCEDURES

The instrumentation and methods used for key components of exhaust emissions are summarized in Table 1. Atomic absorption spectrophotometry was used for trace metal determinations in particulate.

Particulate samples were collected on pure quartz fiber filters after early membrane filters deteriorated from exposure to the high reactivity of the collected sample of catalyst-treated emissions.

Bubbler and impinger samples of the atmospheres were used for collecting ammonia- and sulfur-based gases.

RESULTS

Table 2 lists the concentrations of various engine exhaust components measured during the series of studies of the catalytic converter system. Individual hydrocarbons measured by gas chromatography are shown in Table 3; the aromatic compounds were not measured after it was discovered that those concentrations were so low in the atmosphere of the catalyst-equipped system as to be near or below detection level.

Toxicity Assessment of Mobile Emissions (TAME) studies J and H, were run under the same engine operating conditions; i.e. they were duplicate runs. However, reference to the data of Table 1 shows considerable differences in values between the two runs. When TAME H was performed, the engine was probably not fully broken in, and the catalyst was quite new; the piping system for conducting the emissions to the exposure chambers probably had not yet attained equilibrium conditions of surface exposure characteristics (mainly deposition of particulate and adsorption of organic vapors) for the new engine system. TAME J, run at a later

Table 1. AEROMETRIC CHARACTERIZATION OF EXHAUST EMISSIONS

Pollutant component	Analytic method	Automatic	Manual	Where determined
Carbon monoxide (CO)	Nondispersive infra-red spectroscopy	X		EPM,[*] EC[+]
Total hydrocarbons (THC), as CH_4	Flame ionization spectroscopy	X		EPM, EC
Nitrogen oxides (NO_x includes NO and NO_2)	Chemiluminescence spectrophotometry; colorimetry using Saltzman reagent	X	X	EPM, EC
C_1 to C_5 hydrocarbons (several compounds)	Gas chromatography		X	EC
C_6 to C_{10} aromatic hydrocarbons (several compounds)	Gas chromatography		X	EC
Aldehydes, total	MBTH according to Hauser		X	EC
Particulates, total mass	Filtration gravimetry		X	EC
Particulate size distribution: aerodynamic	Stage impaction (Anderson)		X	EC
Photonomeric	Photoelectronic (Royco)		X	EC
Particulate composition	Infra-red and ultraviolet spectrophotometry		X	EC
Ozone, oxidant	Chemiluminescence spectrophotometry	X		EC

[*] Exhaust or primary exhaust: air mixture.
[+] Exposure chamber.

Table 2. ENGINE EXHAUST EMISSION VALUES FOR CATALYTIC CONVERTER SYSTEM STUDY

		TAME H	TAME I	TAME J	TAME K
Exhaust Dilution Ratio		8/1	9.6/1	8.7/1	9.5/1
CO, ppm:	N-I	7	551	46	40
	I	8	559	41	38
THC, ppm:	N-I	12	110	22	18
	I	13	95	22	18
NO_x, ppm:	N-I	11.0	11.9	12.9	12.6
	I	11.0	5.1	12.6	11.2
NO, ppm:	N-I	8.5	6.7	11.1	10.8
	I	8.0	0.5	9.6	9.7
NO_2, ppm:	N-I	2.5	5.2	1.8	1.8
	I	3.0	4.6	3.0	1.5
Aldehydes, ppm:	N-I	-	10.20	0.08	0.18
	I	-	14.62	0.10	0.11
Methane, ppm:	N-I	-			6.53
	I	-			6.13
Aliphatics: ppm C_4-C_5	N-I	-	1.30	0.61	0.44
	I	-	1.32	0.58	0.39
Olefins: ppm C_2-C_4	N-I	-	13.24	0.89	0.91
	I	-	9.23	0.79	0.82
Acetylene, ppm:	N-I	-	3.28	0.03	0.04
	I	-	3.06	0.03	0.04
Ozone, ppm:	N-I	-	0.0	-	-
	I	-	0.4	-	-
Particulate, mg/m^3	Diluted Exh.	-	1.09	1.10	8.10
	N-I	2.85	0.77	1.08	9.30
	I	2.13	3.59	1.23	8.75

N-I = Nonirradiated atmosphere, exposure chamber with.
I = Irradiated.

Table 3. GAS CHROMATOGRAPHIC MEASUREMENTS OF HYDROCARBONS, ppm

Component	TAME I		TAME J		TAME K	
	N-I	I	N-I	I	N-I	I
n-Butane	0.61	0.61	0.30	0.29	0.21	0.18
i-Butane	0.08	0.08	0.05	0.05	0.03	0.03
n-Pentane	0.20	0.23	0.09	0.09	0.05	0.05
i-Pentane	0.41	0.40	0.17	0.15	0.15	0.13
Acetylene	3.28	3.06	0.03	0.03	0.04	0.04
Ethylene	6.85	5.10	0.82	0.72	0.81	0.74
Propylene	1.81	0.71	0.04	0.04	0.06	0.04
Butane-1	0.26	0.08	Bld	Bld	-	-
Isobutylene	0.63	0.20	Bld	Bld	-	-
1,3-Butadiene	0.41	0.08	Bld	Bld	-	-
Methane					6.53	6.13

Bld = Below level of detection.
N-I = Nonirradiated atmosphere, exposure chamber with.
I = Irradiated.

date, when a more stable system should have been established, was considered to have more accurate atmospheric component values than TAME H. Therefore, the concentration values from TAME J were compared to those from TAME I to evaluate the effect of the catalytic converter on the makeup of the auto exhaust emissions reaching the animal exposure chambers. That comparison is emphasized by the large percentage reduction values of several atmospheric components, which resulted from the use of the platinum- and palladium-coated, pelleted catalyst (Table 4), and by the greatly reduced concentrations of individual hydrocarbons (Table 3).

Since the dilution of the raw exhaust with clean air was not as great in TAME J (8.7/1) as in TAME I (9.6/1), the reduction values listed in the third column of Table 4 were adjusted by a factor appropriate to the differences in dilution values (about 10 percent of the TAME J values) to obtain the more accurate "normalized" values listed in the fourth column.

A barely detectible concentration of platinum (0.029 μg/m^3) was indicated in the diluted emissions of the animal exposure chamber. This result was, of course, for a system using a catalytic converter unit that was quite new and that was shown to be adsorbing a large proportion of the sulfur gases in the exhaust gases.

On the basis of an average flow of 1 m^3/min of raw exhaust produced at a calculated average speed of 35 km/hr (22 mph) on the engine dynamometer, it was estimated that the 0.029 μg Pt/m^3 represented a loss of nearly 0.37 μg Pt/km.

Table 4. COMPARISON OF EXHAUST EMISSIONS, TAME-I AND -J

		TAME-I	TAME-J	% Concentration reduction I → J	Normalized % reduction value
Exhaust Dilution Ratio		9.6/1	8.7/1		
CO, ppm:	N-I	551	46	91.7	92.4
	I	559	41	92.7	93.3
THC, ppm:	N-I	110	22	80.0	81.9
	I	95	22	76.9	79.0
NO_x, ppm:	N-I	11.9	12.9		
	I	5.1	12.6		
NO, ppm:	N-I	6.7	11.1		
	I	0.5	9.6		
NO_2, ppm:	N-I	5.2	1.8		
	I	4.6	3.0		
Aldehydes, ppm:	N-I	10.20	0.08	99.9	99.9
	I	14.62	0.10	99.9	99.9
Aliphatics, ppm: C_4-C_5	N-I	1.30	0.61	53.1	57.7
	I	1.32	0.58	56.1	60.0
Olefins, ppm: C_2-C_4	N-I	13.24	0.89	93.3	93.9
	I	9.23	0.79	91.4	92.2
Acetylene, ppm:	N-I	3.28	0.03	99.1	99.2
	I	3.06	0.03	99.0	99.1
Ozone, ppm:	N-I	0.0			
	I	0.4			
Particulate, mg/m^3					
	Dil'd.Exh.	1.09	1.10		
	N-I	0.77	1.08		
	I	3.59	1.23		

N-I = Nonirratiated atmosphere, exposure chamber with.
I = Irradiated.

If it is estimated that there is 0.04 troy ounce of the noble metal in the catalytic unit (1.244 g), then 0.3×10^{-4} percent of the platinum was lost per kilometer (.62 mile). Such a loss over 80,000 km (50,000 miles) of operation would mean a total loss of 2.5 percent of the platinum originally present.

CONCLUSIONS

The incorporation of the oxidation-type catalyst in the exhaust system resulted in drastic changes in the exhaust emissions:

a. The effectiveness of the catalyst was revealed in the large reduction of carbon monoxide, total hydrocarbons, and various individual organic compounds (such as acetylene).

b. Almost total elimination of aldehydes was achieved.

c. In TAME I (without catalyst), the high value of particulate in the irradiated atmosphere along with the low value of nitric oxide (NO) and the measured presence of ozone indicated that a much greater photochemical reaction of hydrocarbons occurred there than in TAME J (with catalyst). That activity was greater in the case of the olefins than in the acetylene, and negligible for the aliphatics.

d. Gross evidence (color and weight stability) of the particulate in TAME I indicated that the nature of the sample was mainly organic. The particulate in TAME J, on the other hand, was strongly acidic, was liquid in nature, and lost significant weight on standing. Analysis showed sulfate to be the primary constituent. Such facts suggested the presence of sulfuric acid as the major component in TAME J particulate.

SULFATE EMISSIONS RESULTING FROM USE OF HIGH-SULFUR FUEL IN TAME-K

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INTRODUCTION

To supplement the data on exhaust emissions from catalyst-equipped systems in which regular Indolene fuel was used, a high-sulfur content gasoline was substituted in Toxicity Assessment of Mobile Emissions (TAME), study K. In that study, a quantity of thiophene was added to the reference Indolene fuel to provide a sulfur level twice as great (0.10 percent) as that normally present. A more detailed analysis of the particulate was made in order to establish the concentration of sulfate and of the expected high acidity.

EXPERIMENTAL PROCEDURE

The high acidity of the aerosol produced in the exhaust emissions from oxidative catalyst-equipped systems was indicated in preliminary runs of the 350 CID Chevrolet engine. Aerosol collected from an exposure chamber on an electrostatic precipitator plate was a water-white liquid and proved to be very acid by pH-paper test. Also, membrane-type filters used to sample the exposure chamber atmospheres remained an undiscolored white and deteriorated upon standing several hours, sometimes to the point of breaking into fragments.

Therefore, quartz fiber filter material (Pallflex type 2500-QAO) was used to collect aerosol samples at all the sampling points of the piping system. Every filter was weighed immediately after sampling.

Some were weighed again after several hours or overnight standing to allow for equilibration with the room atmosphere and stabilization of the sample weight. Others that were used for aerosol acidity measurements (whole filters or portions) were then placed without delay after the early weighing into a beaker of a specified quantity of distilled, deionized water. At least 30 min was allowed for water extraction of the sample before the initial measurements of conductance and of pH were made. Final measurements of ion concentration were made 16 to 40 hr later.

The aqueous extracts were subsequently used for determination of sulfate ($SO_4^{=}$), ammonium (NH_4^{+}), and nitrate (NO_3^{-}). Sulfate was analyzed by the barium chloranilate method,[1] ammonium by phenolhypochlorite reaction,[2] and nitrate by hydrazine reduction.[3]

Alternate analytical methods were used in some cases to confirm the concentrations determined. A nephelometric method was adapted to sulfate measurement, and an ion specific electrode applied to ammonium measurement. These methods have limited use for the present group of samples because of sensitivity and reproducibility requirements.

Gas samples for nitrate- and ammonium-producing components in the atmospheres were collected by absorption into distilled water or into a weak acid solution. For separation of SO_2 from SO_3, the procedure[1] used was to draw the gas through a bubbler containing isopropanol and then through hydrogen peroxide (H_2O_2) solution or through tetrachlormercurate (TCM) contained in two follow-up bubblers. The ammonium and the nitrate product concentrations were determined by the same methods cited for the aerosol analysis. The SO_3 sulfate in the first bubbler and the SO_2 sulfate in the peroxide bubblers of the three bubbler-train were analyzed by the chloranilate method. The SO_2 in the TCM absorption liquid was analyzed by the West-Gaeke method.[4]

The animal (population) occupancy of an exposure chamber was noted by the number of cages and activity wheels. A cage might contain three adult rats, a litter of recently born rats with their mother, or a group of four hamsters. An activity wheel was associated with a single mouse. A record of the animal occupancy was kept for comparison with levels of ammonium and acidity of the particulate in the atmosphere of the exposure chamber.

RESULTS

A condensation of the analytical values for several ionic components is given in Table 1. Gas and particulate values are listed for the diluted atmosphere sampled immediately after the exhaust pipe and for the atmospheres in each of several exposure chambers.

Total particulate for TAME K is shown in the fourth column of values of Table 2, page 3 of the article, "Effect of Catalyst and of Fuel Sulfur Content Upon Auto Exhaust Emissions." The sulfate value for the diluted exhaust pipe emissions (46.5 $\mu mol/m^3$) in Table 1 of this article represents almost 55 percent of the weight of the total particulate (8.10 mg/m^3). Considering the very highly acidic nature of the aerosol (particulate), one must assume that the sulfate is, most likely, totally sulfuric acid. On the basis of an average emissions volume generated by

TABLE 1. TAME K: ATMOSPHERIC COMPONENT CONCENTRATIONS, μmol/m^3

Component	Exhaust Pipe Emissions Diluted	Exposure (irradiated, 15-10 cages)	Exposure (nonirradiated, 2-0 cages)	Exposure (nonirradiated, no animals	Exposure (irradiated, 4-2 cages + 6 wheels)	Exposure (nonirradiated, 2 cages + 6 wheels)	Exposure (nonirradiated, 12 cages)	Exposure (irradiated, 6 wheels)
GAS:								
(NH_4^+)	-	0.4	0.1	-	0.22	0.33	-	-
(NO_3^-)	-	7.3	2.4	-	8.70	6.25	-	-
($SO_4^=$)	-	15.0	28.0	-	-	-	-	-
(SO_2)	-	2.0	0	-	-	-	-	-
PARTICULATE:								
($2NH_4^+$)	1.6	38.6	4.6	1.1	7.9	21.9	41.2	11.4
(NO_3^-)	0.2	1.2	0	0	0	0.9	0	0.6
($SO_4^=$)	46.5	32.8	34.3	35.0	34.2	31.3	25.5	31.3
($2H^+$)	170.6	0.2	122.9	109.9	54.7	-	0	97.0

the engine of 1 m^3/min, and an average of 35 km/hr (22 mph) equivalent road speed for the engine operation (California cycle), the total particulate value of the diluted exhaust was calculated as approximately 0.13 gm/km.

Actually, the acidity is so high that at the present time, it is unaccountable in terms of the amount of aerosol reported. Further work is required to explain this phenomenon. The point should be made that those filter samples that were not used in the extraction scheme sometimes lost as much as 50 percent of their weight after standing overnight. It was the initial weight upon which the total particulate calculations were made.

Although values are given for (NH_4^+) and (NO_3^-) in the gas phase, (Table 1), it is assumed that the analytical procedures are accounting mainly for ammonia (NH_3) and for the contribution of nitrogen dioxide (NO_2) to these ion centration values. The $SO_4^=$ in most cases is probably a fine mist of acid aerosol in the submicron size range of 0.1 micron or less.

The particulate analyses of Table 1 show that the aerosol in the diluted exhaust pipe emissions (first column) is a highly acid sulfate. The aerosol in exposure chamber No. 15 (second column) is non-acidic and contains ammonium ($2NH_4^+$) nearly quantitative to the sulfate ($SO_4^=$) measured. It is not unreasonable to think, therefore, in terms of the acid (such as sulfuric acid, H_2SO_4) or of the salts such as ammonium sulfate, $(NH_4)_2SO_4$. The amount of sulfate measured in the exposure chambers themselves represented an average of at least 15 percent of the sulfur present in the fuel.

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TAME STUDIES ADDENDA
AEROMETRY DATA FOR TAME L

M. Malanchuk, and J. Burkart

Although the TAME-L test conditions were distinctive in many ways, the results have been listed alongside those of TAME-K to show the similarities and dissimilarities of two tests that at first glance might be considered to be very much alike.

Table I compares the test conditions. TAME-L was a continuous run through 32 days except for a two-hour period each morning when the engine was turned off and the exposure chambers opened to service the test animals for clean-up of chambers and cages and for provision of fresh food and water. That servicing necessitated a cold start-up of the engine at 0800 each day. The automobile engine was a new unit that was substituted for the older one used for TAME-K; that older engine had developed oil leak problems which made it unsuitable for the TAME-L study. The same catalytic converter was used in TAME-L as in TAME-K; however, there was a mechanical vibrator attached to the converter in TAME-L to simulate road vibration during the entire run.

During its nearly 700 hours of use in TAME-L, the catalyst unit gradually increased in outlet temperature of the gas from 760°F to a peak of 1000°F, leveled off at about 985°F and dropped precipitously in temperature when the new supply fuel was introduced into the engine on day 30. That fuel was of lower sulfur content (0.01% S by weight) and of higher aromatics content (32 vol. %). Consequently, much more

Table 1.

Comparison of Test Conditions for TAME-K and TAME-L

	TAME-K	TAME-L
Test Period, Days	7	32
Hours/Day, of Engine Operation	24	22 w. cold start
Fuel	Ref.+thiophene	Ref.+thiophene
Engine	'73 Chev 350 + catalytic conv.	new '73 Chev 350 + catalytic converter
Engine hours accumulated, start-end of run	675-841	32-718
Period of run, hours	166	686
Engine miles accumulated, start-end of run	13500-16820	640-14360
Period of run, miles	3,320	13,720
Catalyst miles accumulated, start-end of run	465-632	774-1460
Catalyst miles accumulated, start-end of run	9320-12640	15480-29200
Total fuel consumed, pounds	1495	6270
Overall averages for the run:		
Fuel, lbs/hr	9.02	9.14
Exhaust oxygen, percent	4.7	3.9
Dilution air flow, scfm	324	335
Dilution ratio	9.5/1	10.2/1
Dilution tube temperature, °F	101°	96°
Catalyst temperature range, °F	835-895	760-1000
Ave. catalyst temperature,, °F	859	892
Exposure chamber temp. & percent R.H.		
Nonirradiated	75°F/60% R.H.	78°F/65% R.H.
Irradiated	75°F/60% R.H.	76°F/66% R.H.

thiophene had to be added to it to bring the sulfur level to the 0.10% concentration maintained in the earlier fuel supply.

With a clean air dilution of the exhaust gases of 10.2/1, an average dilution tube temperature of 95°F was attained as compared to 101°F in TAME-K with its 9.5/1 dilution ratio. Exposure chamber temperatures and relative humidity were a little higher in TAME-L.

Table II compares the test results of TAME-K and TAME-L. The differences in the results appear to emphasize a greater activity of the catalyst or else a lower input from the new engine during the TAME-L run. Carbon monoxide(CO), concentrations were about 1/4 as much in TAME-L as in TAME-K; total hydrocarbons (THC), were about 1/2 as much. Aldehydes, and olefins as represented by ethylene, were considerably reduced in keeping with the THC picture. The lower nitrogen oxide values in a system using the oxidative catalyst could be due to the use of a new engine (conditions).

Total particulate (aerosol) concentration showed a very substantial increase in the dilution tube and in the nonirradiated atmosphere of the system. The irradiated atmosphere had a much smaller degree of increase. However, measurements of sulfate in the particulate indicated a consistently greater proportion of water in the samples from the "nonirradiated" exposure chambers. Much of the increased amount of aerosol in the nonirradiated atmosphere over that in the irradiated atmosphere was due to the greater amount of moisture in the nonirradiated sample. The sulfate content in the irradiated atmosphere filter samples was usually no more than 10 percent lower than that in the nonirradiated atmosphere

TAME-K and TAME-L

		TAME-K	TAME-L
Exhaust Dilution Ratio		9.5/1	10.2/1
CO, ppm			
Exp. Ch:	N-I	40	9.3
	I	38	10.0
THC, ppm, as methane			
Exp. Ch:	N-I	18	10.4
	I	18	9.5
NO_x, ppm			
Exp. Ch:	N-I	12.6	8.9
	I	11.2	8.2
NO, ppm			
Exp. Ch:	N-I	10.8	8.0
	I	9.7	7.0
NO_2, ppm			
Exp. Ch:	N-I	1.8	0.9
	I	1.5	1.2
Aldehydes, total, ppm			
Exp. Ch:	N-I	0.18	0.02
	I	0.11	0.05
Formaldehyde, ppm			
Exp. Ch:	N-I		
	I		
Aliphatics, ppm, C_2-C_5			
Exp. Ch:	N-I	0.44	0.29
	I	0.39	0.26
Methane, ppm			
Exp. Ch:	N-I	6.53	6.19
	I	6.13	6.13
Olefins, ppm, ethylene			
Exp. Ch:	N-I	0.81	0.07
	I	0.74	0.06
Acetylene, ppm			
Exp. Ch:	N-I	0.04	-
	I	0.04	-
Particulate, mg/m^3			
Dilution Tube		8.10	21.56
Exp. Ch:	N-I	9.30	17.13 (~35% SO_4)
	I	8.75	11.85 (~47% SO_4)

samples. Specifically, out of 15 simultaneous samplings that were taken from the "nonirradiated" and "irradiated" exposure chambers in TAME-L and those samplings were also checked for sulfate content (such paired samplings were taken daily, but not all were analyzed for sulfate), every "irradiated" sample was higher in sulfate (sulfuric acid) concentration than the "nonirradiated" sample with but one exception--a case of the (nearly) same amount of sulfate per less amount of total particulate giving a higher concentration reading for the sulfate. This finding resulted from having the same amount of sulfate in a smaller amount of total particulate which would give a higher sulfate value per unit of particulate. Accuracy of the particulate measurements could be significantly improved with availability of a temperature + humidity controlled room devoted to the weighing of these humidity-sensitive samples.

A plot of the day-to-day particulate concentrations at three different points in the test exposure system, Figure 1, shows a steady drop during the period until the very end when a sudden rise occurred after a supply of new Indolene fuel had to be introduced in order to extend the study a few more days. The same trend is seen in the atmosphere drawn from each of the three sampling points - the dilution tube, the exposure chamber with the non-irradiated atmosphere, and the exposure chamber with the irradiated atmosphere.

The CO, THC, and NO_x NO-NO_2 values for TAME-L in Table II are mean values for the 32-day study based on the computer tape values recorded during the 22-hour, engine-on period.

Various analytical methods used to measure platinum and palladium in the filter samples collected from the diluted exhaust emissions during the California 7-Mode cycle runs were inclusive in establishing the amounts of those two elements in the emissions. Concentration values obtained by atomic absorption spectrophotometry yielded emission values calculated as 0-1.2 μg Pt/km (0-2 μg Pt/mi). Techniques using nuclear energy sources to induce UV fluorescence yielded values of a decade or two as great for the platinum and also for palladium.

THE INHALATION TOXICOLOGY OF AUTOMOTIVE EMISSIONS AS AFFECTED BY AN OXIDATION EXHAUST CATALYST

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R. Miller and J. F. Stara

INTRODUCTION

This report presents data from a series of acute animal exposure studies which were designed to assess certain health hazards of automobile exhaust from engines equipped with or without oxidative catalytic converters. It is expected that these catalytic converters will be widely used by the automobile manufacturers in order to control exhaust emission levels of carbon monoxide (CO) and hydrocarbons (HC). The concern, of course, is that use of these devices might release some other noxious or toxic substances into the environment. Three studies are discussed in this report: TAME I, J, and K. (TAME is an acronym used by us which means toxicologic assessment of mobile emissions). TAME I was a study of the biological effects of whole exhaust from an automobile engine with no catalyst, which served as a reference or baseline study; TAME J was identical except for the addition of an oxidative catalyst to the exhaust train; TAME K had the catalyst plus additional organic sulfur compounds added to the fuel to maximize production of sulfate emissions. (This paper has been submitted to Environmental Health Perspectives for publication.)

EXPERIMENTAL METHODS AND RESULTS

A. Exposure System. The exhaust emission generation system used in these studies consisted of a 1973 Chevrolet 350 CID production engine equipped with exhaust gas recirculation (EGR), air pump, and turbohydramatic transmission coupled to an "eddy current" absorption dynamometer. In each study, the engine system was run continuously for 7 days on a modified "California" control cycle (Table I). The gasoline used in the Chevrolet engine as a reference fuel was American Oil Co. unleaded 91 Octane Test Fuel, Intermediate Grade Indolene Clear (Table II). Note that in TAME K, thiophene was added to the reference fuel to produce a high sulfur fuel (1000 ppm). Some of the engine operating conditions are summarized in Table III.

In TAME J and K, the exhaust passed through a noble metal pelletized type oxidation catalyst (manufactured by Engelhard Co. to General Motors specifications) and a muffler before mixing with CBR filtered and conditioned air in a dilution tube. The diluted exhaust was piped to a large volume mixing chamber and then entered dynamic flow irradiation chambers lighted to simulate sunlight so that photochemical reactions might occur. The irradiated exhaust then entered animal exposure chambers. Additionally, the system provided nonirradiated exhaust in the same concentration to other exposure chambers. In each study there were clean air atmospheres and in TAME I there was a CO atmosphere for control animal exposures. The catalyst was removed from the system for the TAME I exposure.

Aerometry. The major components characterized in the exhaust emissions and methods used are summarized in Table IV. Particulate samples were collected on pure quartz fiber filters. Bubbler and impinger samples of the atmospheres were used for collecting ammonia and sulfur based gases.

The concentration in the exposure chambers of the various emission components are shown in Table V. The incorporation of the oxidation

TABLE I

Modified "California Cycle" Used in the Fuel Emission Studies

Mode	Speed, M.P.H.	Time, Seconds
Idle	0	20
Acceleration	0 to 30	14
Cruise	30	15
Deceleration	30 to 15	11
Cruise	15	15
Acceleration	15 to 49	29
Peak	49 to 50	1.5
Deceleration	50 to 0	31.5
	Total	137 sec.

TABLE II

Comparison and Product Analysis of the Gasoline Used for Exhaust Emission Studies

Shipment Number	#1	#2
Date Delivered	3/30/73	10/29/73
Quantity, gallons	2,000	1,500
Octane Number, research	91.4	91.3
Octane Number, motor	82.9	82.5
Lead Atm. Abs., gm/gal.	0.01	0.01
Phosphorus, gm/gal.	0.002	0.00
Sulfur, wt. %	0.04	0.05
Aromatics, Vol. %	25.4	23.5
Olefins, Vol. %	11.8	9.9
Gum, Existent, mg/100 cc	0.8	1.0
Gravity, °API	61.4	61.5
Oxidation Stability, minutes	600+	600+
Ried Vapor Pressure, lbs.	9.1	9.0

Note: Shipment #1 used for studies I and J.
Shipment #2 used for study K with Thiophene added to produce 0.10% by weight sulfur.

TABLE III.

Comparison of Engine Operating Conditions

	TAME I	TAME J	TAME K
Fuel	Ref. only	Ref. only	Ref. + Sulfur
Engine	'73 Chev. No catalyst	'73 Chev. w/catalyst	'73 Chev. w/catalyst
Engine hours	255-425	444-615	675-841
Study hours	170	171	166
Engine miles	8,500	12,300	16,820
Cumulative Catalyst hours		465	632
Catalyst miles		9,300	12,640
Total Fuel (lbs)	1,545	1,601	1,495
Fuel, lbs/hr.	9.08	9.40	9.02
Exhaust Oxygen (%)	N.A.	4.2	4.7
Air/Fuel Ratio	14.4 cycling 12.4 idle	-	-
Oil Consumption, qts.	1/2	1/4	1/4
Dilution Ratio	9.6/1	8.7/1	9.5/1
Dilution Air Flow Average, SCFM	305	310	324
Dilution Tube Temperature Average, °F	101	114	101

TABLE IV

Characterization of Exhaust Emissions

Pollutant component	Analytic method	Where determined*
Carbon monoxide (CO)	Nondispersive Infra-red spectroscopy	EPM, EC
Total hydrocarbons (THC), as CH_4	Flame ionization spectroscopy	EPM, EC
Nitrogen oxides (NO_x includes NO and NO_2)	Chemiluminescence spec.; colorimetry using Saltzman reagent	EPM, EC
C_1 to C_5 hydrocarbons (several compounds)	Gas chromatography	EC
C_6 to C_{10} aromatic hydrocarbons (several compounds)	Gas chromatography	EC
Aldehydes, total	MBTH according to Hauser	EC
Particulates, total mass	Filtration gravimetry	EC
Particulate size distribution:		
Aerodynamic	Stage impaction (Anderson)	EC
Photonomeric	Photoelectronic (Royco)	EC
Particulate composition	Infra-red and ultra-violet spectrophotometry	EC
Ozone, "oxidant"	Chemiluminescence spec.	EC

*EPM - Exhaust or primary exhaust: air mixture;
EC - exposure chamber

TABLE V

Engine Exhaust Emission Values for Selected Components in the Animal Exposure Chambers

		TAME I	TAME J	TAME K
Exhaust Dilution Ratio		9.6/1	8.7/1	9.5/1
CO, ppm:	NI[a]	651	46	40
	I[b]	559	41	38
THC, ppm:	NI	110	22	18
	I	95	22	18
NO_x, ppm:	NI	11.9	12.9	12.6
	I	5.1	12.6	11.2
NO, ppm:	NI	6.7	11.1	10.8
	I	0.5	9.6	9.7
NO_2, ppm:	NI	5.2	1.8	1.8
	I	4.6	3.0	1.5
Aldehydes, ppm:	NI	10.20	0.08	0.18
	I	14.62	0.10	0.11
Aliphatics, ppm: C_4-C_5	NI	1.30	0.61	0.44
	I	1.32	0.58	0.39
Olefins, ppm: C_2-C_4	NI	13.24	0.89	0.91
	I	9.23	0.79	0.82
Acetylene, ppm:	NI	3.28	0.03	0.04
	I	3.06	0.03	0.04
Ozone, ppm:	NI	0.0	-	-
	I	0.4	-	-
Particulate, mg/M^3	NI	0.69	0.96	6.53
	I	3.19	1.09	5.85

[a] NI = nonirradiated exhaust

[b] I = irradiated exhaust

catalyst into the exhaust system resulted in a large reduction in CO, total HC, and various individual organic compounds. In TAME I, the photochemical reactions in the irradiated atmospheres were very pronounced as evidenced by the presence of ozone, the low value for NO, and the high value for particulate. The color and weight stability suggested the particulate to be organic in nature. In TAME J and K, the particulate was strongly acidic, was liquid in nature, lost significant weight on standing and contained sulfate as a primary constituent. All of this suggested sulfuric acid as the major particulate component.

C. Biologic Systems and Effects

1. Infant mortality and body weight determinations: Groups of 10 lactating female outbred albino rats and their 2-week old offspring (10 suckling rats/litter) were exposed to each of the treatment atmospheres for 7 days. Animals were weighed at the beginning and end of the study. Infant mortality was noted on a daily basis. As may be seen from Table VI, there was a prominent effect on infant mortality in those animals exposed to exhaust in TAME I. This was obviously not a CO effect alone, but rather due to the combination of biologically active pollutants. A parallel effect was noted as far as body weight changes (Table VII) in both the adult and suckling animals. In TAME J and K, there were not pronounced treatment effects on either of these parameters.

2. Clinical pathology determinations: Groups of 25 adult male outbred albino rats were exposed to each treatment atmosphere. Five animals per treatment were removed on days 2 - 6 of the study,

TABLE VI

Survival of Suckling Rats Following Exposure to Whole Automobile Exhaust

	TAME I	TAME J	TAME K
Clean air control	100%	98%	100%
Nonirradiated exhaust	23%	100%	100%
Irradiated exhaust	0%	100%	100%
Carbon monoxide control	96%		

TABLE VII

Daily Change in Body Weight (grams) in Rats During Exposure to Whole Automobile Exhaust

		TAME I	TAME J	TAME K
Lactating Female Rats:	CA[a]	+ 2.2	+ 2.9	+0.8
	NI[b]	- 6.7	- 0.2	+2.2
	I[c]	-11.7	- 1.3	+4.6
	CO[d]	+ 0.4		
Suckling Rats:	CA	+ 2.0	+ 2.0	+ 2.1
	NI	- 0.6	+ 1.9	+ 2.6
	I	—	+ 2.1	+ 3.3
	CO	+ 1.3		

a: Clean Air Control Atmosphere
b: Nonirradiated Exhaust Atmosphere
c: Irradiated Exhaust Atmosphere
d: Carbon Monoxide (550 ppm) Control Atmosphere

anesthetized, and exsanguinated by abdominal aorta catheterization. The clinical laboratory determinations and treatment means are shown in Tables VIII-XI. Again a treatment effect if present occurred only in TAME I in the exhaust exposure groups with the more prominent changes in the animals exposed to irradiated exhaust. The high CO levels had some effect on the hematologic parameters but was not totally responsible. It should be further noted that the high CO levels produced a rather striking increase in hemolysis resistant red blood cells which necessitated manual determinations of white blood cell counts. No treatment effect was noted in TAME J or K. Because of the historical association of platinum with allergic responses, it was particularly interesting to note no increase in eosinophils in TAME J or K.

3. Tissue chemistry determinations: Samples of lung, liver and kidney were collected from animals exposed to the exhaust atmospheres for determination of platinum (Pt) and palladium (Pd). The tissue samples were lyophilized and wet digested using aqua regia with all nitric acid fumes being eliminated by other additions of hydrochloric acid and subsequent heating. The digested samples were transferred with hydrochloric acid and deionized water to a volumetric flask with an acid concentration of 10%. After the samples were treated with potassium iodide, the metals were concentrated by organic extraction using methyl-isobutyl ketone. Fifty microliter aliquots were analyzed using a Perkin-Elmer 503 Atomic Absorption Spectrophotometer equipped with a GHA 2000 Graphite Furnace.

TABLE VIII

Treatment Mean Values for Selected Hematologic Parameters in Male Rats

		TAME I	TAME J	TAME K
RBC/cmm (x 10^6):	CA	7.07	7.14	
	NI	7.62	7.00	
	I	7.78	7.07	7.01
	CO	7.44		7.21
WBC/cmm (x 10^3):	CA	9.1	9.3	
	NI	11.9	9.0	
	I	12.0	8.7	9.4
	CO	15.7		8.8
Lymphocyte:neutraphil Ratio:	CA	5.3	5.3	
	NI	1.7	5.1	
	I	1.0	5.3	4.8
	CO	2.3		4.9
HB (gm %):	CA	14.9	14.6	
	NI	16.5	14.7	
	I	16.7	14.5	14.5
	CO	15.2		14.7
HCT (%):	CA	41.6	40.8	
	NI	46.6	41.0	
	I	47.4	40.1	40.4
	CO	43.2		41.0

TABLE IX

Treatment Mean Values for Selected Blood Chemistry Parameters in Male Rats

		TAME I	TAME J	TAME K
Total serum protein (gm%):	CA	6.0	5.8	
	NI	6.3	6.1	6.2
	I	6.8	6.0	6.2
	CO	6.3		
Alkaline phosphatase (U):	CA	79.1	80.9	
	NI	54.2	91.4	94.5
	I	40.8	83.4	89.8
	CO	79.4		
SGOT (R-F units):	CA	161.6	169.7	
	NI	185.3	174.4	161.8
	I	196.7	174.8	162.8
	CO	175.2		
SGPT (R-F units):	CA	48.5	40.0	
	NI	60.5	40.7	47.2
	I	53.7	42.0	46.4
	CO	45.8		
BUN (mg%):	CA	23.8	22.5	
	NI	21.0	21.8	19.1
	I	28.3	21.4	19.4
	CO	20.0		

TABLE X

Treatment Mean Values for Selected Coagulation Tests in Male Rats

		TAME I	TAME J	TAME K
Platelets/cmm (x 10^6):	CA	0.95	0.93	
	NI	1.07	0.97	1.02
	I	1.10	0.92	.98
	CO	1.08		
Fibrinogen (mg/dl):	CA	170	175	
	NI	165	175	177
	I	220	170	175
	CO	160		
Prothrombin time (seconds):	CA	12.5	12.2	
	NI	12.9	12.1	12.2
	I	12.6	12.3	12.2
	CO	12.3		
Partial thromboplastin time (seconds):	CA	19.9	19.9	
	NI	21.7	19.3	19.1
	I	22.4	19.2	18.7
	CO	21.3		

TABLE XI

Treatment Mean Values for Selected Serum Electrolytic Constituents in Male Rats

		TAME I	TAME J	TAME K
Na^+ (meg/l.):	CA	133.2	140.8	
	NI	136.6	141.0	142.2
	I	135.7	141.2	142.8
	CO	142.6		
K^+ (meg/l.):	CA	4.8	5.3	
	NI	5.0	5.5	5.3
	I	5.2	5.4	5.6
	CO	5.2		
Cl^- (meg/l.):	CA	103.2	105.6	
	NI	104.4	104.8	105.2
	I	102.1	105.2	104.2
	CO	106.2		
Ca^{++} (meg/l.):	CA	4.9	4.4	
	NI	5.0	4.6	4.6
	I	4.9	4.5	4.7
	CO	4.7		

The lower limits of detectability for total Pt and Pd in a gram of tissue were 0.2 and 0.1 μg, respectively. No Pt or Pd could be detected in any of the tissue samples from TAME I, J, or K.

4. Morphologic pathology determinations: Tissues from adult outbred albino rats and adult male golden Syrian hamsters exposed to each treatment were collected and fixed in 10% formalin. Specimens of lung, liver, and kidney were processed, paraffin embedded, sectioned, hematoxylin and eosin stained, and examined microscopically for evidence of morphologic changes attributable to the exposure.

There were no treatment related changes in TAME J or K. In TAME I, however, there were extensive pulmonary changes which were more severe in hamsters and most severe in those animals exposed to irradiated exhaust. In the nonirradiated exhaust group, the pulmonary changes were relateable to the levels of NO_2, with an increase in alveolar macrophages at the level of terminal bronchioles initially, followed by a proliferative phase with some apparent increase in epithelialization of respiratory ductules, and in thickness of alveolar septae. In the hamsters exposed to irradiated exhaust there was a very severe acute purulent bronchitis and bronchiolitis which progressed to a subacute purulent bronchopneumonia by the end of the study. Additionally, there were some degenerative changes in renal and hepatic tissue by the end of the study in these animals. The only lesion which could be solely related to CO levels was extramedullary hematopoiesis in the liver of the rats after 4 days exposure.

DISCUSSION

The initiating force behind use of the oxidative catalytic converter in the automobile exhaust train is the emission standards for CO and HC as set forth in the Clean Air Amendments of 1970.[1] The aerometry findings in this study would suggest that there is in fact a very marked reduction in CO and HC levels due to the use of the catalyst.

It was further expected that the oxidative catalysts would have minimal effect on NO_x levels, which again was corroborated by these studies. The catalyst did have an indirect effect in the exposure system used in these studies on levels of NO_2 and other oxidants (i.e. ozone) which constitute some of the more biologically active exhaust compounds relative to biological effects. The reasons for this relate to findings that at HC/NO_x ratios less than 3:1, no free oxidant is formed. These same HC/NO_x ratios have a similar effect on NO_2 levels due to the overall NO-NO_2 reaction systems. In TAME I, the HC/NO_x ratio was about 9:1; in TAME J and K the ratios were about 1.5 - 2:1. This then helps explain the pronounced reduction in acute toxicity associated with the exposures, rather than the lower levels of CO alone.

As noted, the oxidation catalyst did have an effect on the type of particulate with an increase in the acidic fraction (probably sulfuric acid). There were not any demonstrable acute biological effects in any of the animals studied, which were attributable to these altered particulates. The study did not rule out possible chronic effects due to long-term exposure either as a result of the increased sulfate emissions or attrition products of the noble metal oxidation catalyst. It is therefore imperative that long-term studies be initiated to provide this additional information.

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PULMONARY MICROSOMAL MIXED FUNCTION MONOOXYGENASE ACTIVITY FOLLOWING EXPOSURE TO CATALYTICALLY-TREATED AUTO EXHAUST

L. L. Hall, I. Washington, J. Adams, K. Campbell, Y. Yang, and W. Moore

INTRODUCTION

The lung serves as a primary target organ for many air pollutants because it is a major portal of entry for atmospheric contaminants. Chemical carcinogenesis is of considerable concern in relation to environmental pollutant exposure either by carcinogen or co-carcinogen exposure. The association of microsomal mixed function monooxygenase with carcinogenesis[1] suggested the determination of effects of catalytically-treated auto exhaust on this system.

METHODS

Three hundred and sixty (360) adult male Syrian hamsters weighing 121.29 ± .055* gms were randomized into four studies with three treatments per study. Two studies (I,III) were performed on non-induced animals, and two studies (II, IV) were performed on hamsters where cytochrome P-450 was induced with benzo(a)pyrene (BaP) (25 mg/kg intraperitoneal) twenty-four hours prior to sacrifice. Studies I and III were performed on hamsters exposed continuously for five days to one of the following atmospheres: 1) clean air (CA); 2) nonirradiated (NI); 3) irradiated (I) exhaust. Studies II and IV were performed the same except for induction on day five and sacrificed twenty-four hours later. The animals were exposed to the test atmospheres during the induction phase.

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*Coefficient of variation

The hamsters were anesthetized (IP) with pentobarbital, exsanguinated by cutting the heart, and the lungs removed _in toto_ and quickly immersed in cold saline (4°C). The lungs from three animals were then trimmed of bronchi, and connective tissue weighed, and placed in cold 0.15 M KCl for homogenization with a Willems Polytron. Mixed function monooxygenase activity (AHH) was assayed as described by Dixon _et al._ (1970) [2] where the fluorescence of the phenolic metabolite is used as an indicator of BaP metabolism. Homogenate concentration of 25 mg tissue/ml and a sixty minute incubation period were used. The results are expressed as the fluorescence equivalent to picomoles of 3-hydroxybenzopyrene formed per minute per mg tissue protein.

RESULTS

Table 1 shows the effect of the experimental atmospheres on hamster body weight and the lung weight-body weight (lw/bw) ratios. A statistically significant increase (3.94%) in the lw/bw ratio was noted in the non-induced animals exposed to irradiated exhaust for the five day experimental period. No significant effects in the body weight or lw/bw ratios were noted in either the induced hamsters or animals exposed to nonirradiated exhaust.

Table 2 shows the effect of auto exhaust on the levels of AHH as reflected by fluorescent phenolic compounds. A statistically significant ($p = .05$) reduction in basal activity was found in studies I and III (non-induced) amounting to 18.59 and 12.13 percent, respectively, following five days exposure to irradiated exhaust. No effect was noted in the induced animals or the non-induced animals exposed to nonirradiated exhaust.

Table 1

Changes in Body Weight and Lung Weight/Body Weight Ratios Following Exposure to Catalyst-treated Auto Exhaust

Experiment	Treatment	No. of Animals	Body Weight*	LW/BW*
Non-induced	Clean air controls	60	120.98 (.08)	0.48835 (.05)
	Nonirradiated exhaust	60	119.15 (.10)	0.48986 (.05)
	Irradiated exhaust	60	121.90 (.09)	0.50758 (.06)**
Induced	Clean air controls	60	122.00 (.08)	0.49196 (.05)
	Nonirradiated exhaust	60	121.75 (.08)	0.49250 (.06)
	Irradiated exhaust	60	121.97 (.09)	0.49268 (.06)

* Number in brackets is coefficient of variation

** Significantly different from controls at $p = .05$ level

Table 2

Effect of Catalyst treated Auto Exhaust on Hamster Aryl Lung Microsomal monooxygenase With and Without Induction

Study	Treatment	Sample Size	Mean	Var.	Cu
1 (without induction)	Clean Air	10	0.27942	.00173	
	Nonirradiated exhaust	10	0.28298	.00099	
	Irradiated exhaust	10	0.22747*	.00088	.132
2 (with induction)	Clean Air	10	.83320	.01606	
	Nonirradiated exhaust	10	.82379	.01422	
	Irradiated exhaust	10	.77183	.00636	.136
3 (without induction)	Clean Air	10	.24443	.00109	
	Nonirradiated exhaust	10	.26376	.00128	
	Irradiated exhaust	10	.21479**	.00116	.142
4 (with induction)	Clean Air	10	0.76066	.00562	
	Nonirradiated exhaust	10	0.77262	.01237	
	Irradiated exhaust	10	0.70457	.00719	.122

* CA = NI > I at p = .05 level

** NI >I; CA = NI; CA = I at p = .05 level

DISCUSSION

Due to the length of this study, repeat experiments using the five day exposure protocol were employed to determine the effect on the basal levels of microsomal P-450 activity and also if exposure to auto exhaust affected the hemoprotein induction phase. In addition it was possible to perform repeated studies to ascertain the effect variability in a controlled fashion. The depression noted following exposure to irradiated exhaust is consistant with our previous experience. The increase in sample size and dual experiments confirm the existance of the depressive effect, its repeatability , and our ability to detect the change. Although the depression is not large, it is real and based on our previous studies, some speculation is possible regarding its causation. Previous experiments have suggested an inverse relationship between AHH activity and total hydrocarbon, NO_2, aldehydes and olefins. However, the increased particulate in this study could be a contributor if it contains a significant amount of H_2SO_4 since the levels of the other components are quite low. No studies on the effect of H_2SO_4 aerosol have been published so this hypothesis is purely speculative and arrived at by default.

The increase in lung weight-body weight ratio which was not found in other catalytic studies, is further suggestive evidence for a particulate effect since this study showed the largest particulate loading of any of the previous studies. Further research is necessary to resolve this question.

The biological impact of the reduction is microsomal mixed function monooxygenase following exposure to auto exhaust is uncertain at this time. The experimental data available as to how AHH relates to chemical carcinogens is unclear, but this may be resolved in the near future.[1,2]

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BIOCHEMICAL EFFECTS OF EMISSIONS FROM AN AUTOMOBILE ENGINE WITH AND WITHOUT CATALYTIC CONVERTER

S. D. Lee, V. N. Finelli, L. McMillan, and R. M. Danner

As a part of the toxicological studies of automobile engines with and without catalytic converters, the Biochemistry Section, in collaboration with Dr. Finelli of the Department of Environmental Health at the University of Cincinnati, has studied early biochemical alterations in rats exposed to auto exhaust emissions.

MATERIALS AND METHODS

Experimental Animals

Each exposure experiment consisted of 30 female Sprague-Dawley rats, each animal weighing approximately 200 g, divided into three groups of 10 animals: Clean Air (CA), non-irradiated (NI), and irradiated (I).

Exposure Conditions

The exposure system has been described by Hinner et al.[1] The concentrations of major exhaust components in the exposure chambers have been described by Malanchuk et al.[2] Temperature and humidity in the exposure chambers were kept constant throughout the experiment at 22°C and 50 percent relative humidity, respectively. The exposures were conducted 24 hr a day, for 7 consecutive days. Two animal exposure experiments were conducted using the exhaust from the same engine with and without the catalytic converter. In addition, an experiment was performed by exposing a group of animals to carbon monoxide alone (experiment CO) at a concentration of 575 mg/m^3 (500 ppm), which approximately reflects the carbon monoxide level observed in exposure chambers when emissions from the engine without the catalytic converter was tested.

The following parameters were determined: hematocrits, serum lactate dehydrogenase (LDH), serum glutamic oxaloacetate transaminase (SGOT), and serum lysozyme. Serum LDH and GOT were determined using DADE reagent sets (American Hospital Supply Corp., Miami, Fla.), and lysozyme was assayed with Worthington kits (Worthington Biochemical Corp., Freehold, N. J.). Blood samples were obtained from animals by tail vein puncture.

RESULTS AND DISCUSSION

Figure 1 shows the drastic effects on the hematocrit of the exposure to emissions from the engine without the catalytic converters. At the end of the 7-day exposure, very high hematocrit levels were observed in the experimental animals: 62.3 ± 1.5 percent for NI, and 66.2 ± 0.5 percent for I, as compared to a normal value of 43.2 ± 0.9 percent for the clean air group. During a recovery period of 3 weeks, the hematocrit values were obtained weekly, and a gradual return to normal was seen in the animals of both NI and I groups. The animals exposed to carbon monoxide showed an average hematocrit of 62.5 ± 0.9, which is equal to the value found for the NI group in the experiment without a converter.

The hematocrit in the animals exposed to emissions from the engine equipped with a catalytic converter did not differ from control values. From the above data, it seems that the elevation of the hematocrit is due to the carbon monoxide concentration in the exposure chambers. The

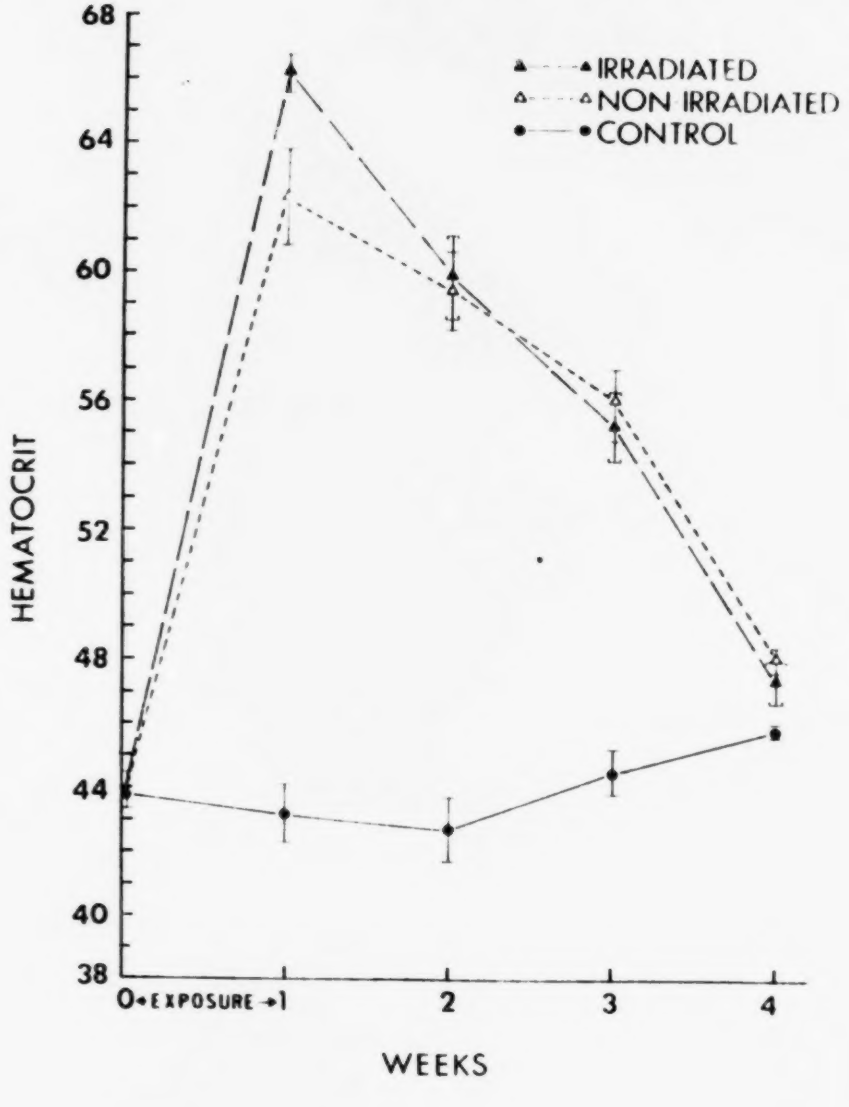

Figure 1. Hematocrit levels in animals exposed to engine emissions without catalytic converter

levels of carbon monoxide in NI and I groups in the experiment without the catalytic converter were 551 and 559 ppm, respectively; and for NI and I groups with the catalytic converter, the carbon monoxide levels were reduced to 46 to 41 ppm. The increased hematocrit may be due to polycythemia and/or dehydration. Total serum protein or albumin analyses were not obtained, and therefore the occurrence of dehydration cannot be confirmed; however, the data collected from histological examination of the experimental animals[3] revealed the presence of large numbers of ruptured red blood cells, which may indicate a polycythenic response.

To assess organ damage in exposed animals, the activity of LDH, GOT, and lysozyme in serum was assayed. These intracellular enzymes are characteristic of appropriate organs, and an increase of enzymatic activity in serum would indicate, presumably, a leakage of enzymes from injured cells. SGOT was not significantly elevated in any of the exposed animals, a fact that would indicate that neither liver nor heart were damaged by exposure to various types of emissions and to carbon monoxide. Serum LDH was elevated in the animals exposed to emissions from the engine without a catalytic converter. Figure 2 shows that at the end of the exposure period, the animals from both NI and I groups showed approximately a 200-percent increase in serum LDH activity. In the recovery period, while the NI group values tended to return to normal, the I group values presented an unexplained erratic behavior; moreover we cannot explain the low value obtained in the third week for the CA group. No significant changes in LDH activity were observed in the experimental animals when

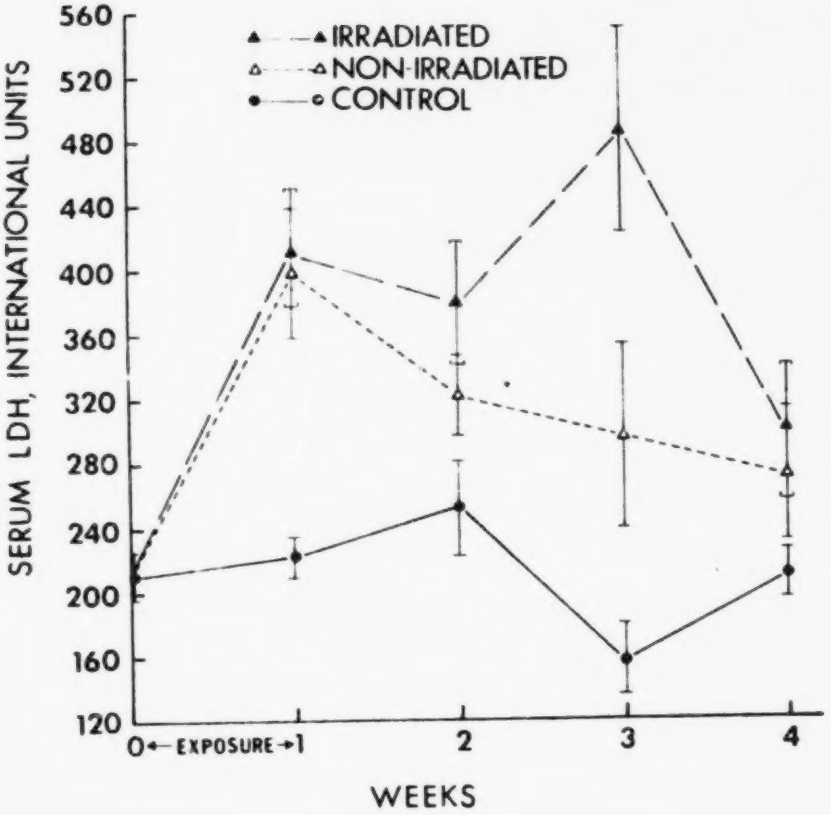

Figure 2. Serum LDH activities in animals exposed to engine emissions without catalytic converter

the converter was used, or when they were exposed to CO. Serum lysozyme activity was not assayed in the experiment conducted without a catalytic converter; however, in the experiment with a converter, the exposed animals did not show any statistically significant elevation. From the above preliminary results, it appears that the target organs of the toxic components present in the emissions from engines without catalytic converters are probably the lungs and/or kidneys.

The introduction of catalytic converters into the automobile exhaust system not only has reduced the levels of certain exhaust constituents, but has effectively decreased or eliminated the biological effects studied.

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MORPHOLOGICAL EFFECTS OF EXPOSURE TO WHOLE EXHAUST EMISSIONS FROM AN AUTOMOBILE ENGINE EQUIPPED WITH A NOBLE METAL CATALYST

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and

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INTRODUCTION

A contract (No. 68-03-0295) was let to Batelle Columbus Laboratories for morphological examination of lung tissues from hamsters exposed in the TAME L study. The exposure criteria and aerometry for TAME L are given in other reports in this document (TAME STUDIES ADDENDA - Aerometry Data for TAME-L). This study was designed to determine whether detectable changes were evident in the airways of hamsters exposed to irradiated and nonirradiated catalytic treated auto emissions. Light microscopy and scanning electron microscopy were used to evaluate morphologic characteristics.

METHODS

For this study, 5 hamsters were sacrificed from each of the following groups:

Group I - nonirradiated exhaust, 14-day exposure
Group II - irradiated exhaust, 14-day exposure
Group III - control air, 14-day exposure
Group IV - nonirradiated exhaust, 27-day exposure
Group V - irradiated exhaust, 27-day exposure
Group V - irradiated exhaust, 27-day exposure
Group VI - control air, 27-day exposure

Each animal was anesthetized with sodium pentabarbital ip, heparinized, and trachea exposed and cannulated. The lungs were fixed in situ under pressure with Karnovsky's for 30 minutes and excised and fixed an additional 60 minutes. The lungs were then rinsed free of extraneous fixative and placed in cold buffer for transporting to Battelle. In the Battelle-Columbus laboratories, part of the lung (superior right lobe) was prepared for scanning electron microscopy and part for light microscopy. All SEM evaluations were performed with a Cambridge Mark II stereoscan instrument with beam accelerating voltages of 20 mv. A total of 434 photomicrographs was taken of fine-structural detail from 122 tissue fragments for evaluation.

RESULTS

Scanning Electron Microscopy

Only minor differences could be identified between specific groups of exposed hamsters, and no areas were found in any bronchiolar surface which could be considered to represent significant lesions or sites of major evidence for injury. This general observation was also supported by the evaluation of light microscopy sections.

Such differences as were observed were considered to be subjective assessments of relatively limited areas of the bronchiolar surface areas under higher magnification. Variation in surface topography from site to site was characteristic of all bronchiolar surfaces examined. Marked variations between samples from the same lung, and between animals of the same group, were also observed. Exposure to the irradiated and non-irradiated exhaust appeared not to have impaired the functional integrity of the bronchiolar surfaces to a level sufficient to exert substantial structural and morphological changes, or to result in sites of frank lesions.

Histology

There was a moderate degree of variability in morphologic features of bronchiolar epithelium among bronchioles within a given lung, and among lungs from different animals. The bronchiolar epithelium was generally columnar to cuboidal with flattened epithelium evident in limited areas of bronchioles from several specimens, including those from control groups. Bronchiolar epithelium was generally one cell layer thick although two or more layers were occasionally visible. There was a "piling up" of bronchiolar epithelial cells in most specimens examined. This appearance possibly results from contraction of the bronchiole at death or during processing. Cellular protrusions were evident in nearly all specimens examined being more prominent in some sections than others. These protrusions probably represent the nonciliated cells described above and seen in the SEM photomicrographs. There was generally a decrease in numbers of cilia in the smaller bronchioles. Cilia at all levels were irregular in distribution as judged by histologic appearance. There was moderate variation in appearance and distribution of cilia within bronchioles of a given specimen, and this variation was generally consistent throughout all specimens examined.

The only lesions observed were minor and were noted in animals from control groups as well as exposed groups. These lesions consisted of small foci of mononuclear cell accumulations on the visceral pleura, small foci of mononuclear cell accumulations adjacent to bronchioles, in one instance a collection of neutrophils in 3 adjacent alveoli. These changes, due to their nature and the fact that they appeared in control groups with frequency similar to that of exposure groups. Changes correlatable to the variations described from SEM evaluations were not observed.

AUTO EXHAUST TOXICITY AND THE REMOVAL OF PARTICULATE FROM THE LUNG-- CATALYTIC CONTROL DEVICE STUDIES

L. Hall, J. Adams, I. Washington, K. Campbell, Y. Yang, and W. Moore

INTRODUCTION

The pulmonary route with a surface area of approximately $70 m^2$ is the major portal of entry for atmospheric pollutants and therefore the first site where toxic effects can occur. Self-cleansing mechanisms are necessary for maintaining the overall integrity of this system. Intoxicants which alter this system can therefore have a profound effect on the ability of the organ to perform its physiological role. In order to assess the effect of auto exhaust pollutants on this system, a challenge test using an inert particulate, titanium dioxide, for assessing the physiological state of the protective mechanisms was performed on hamsters exposed to nonirradiated and irradiated auto exhaust.

METHODS

One hundred thirty five (135) adult male Syrian hamsters weighing approximately 120 gms were randomized into three treatment groups (45 each) with three subsets (15/set) per group. Following seven days exposure to auto exhaust under conditions described by Hinners and Malanchuk (see this report), the hamsters were exposed to a test atmosphere of titanium dioxide at a mean concentration of 16.4 mg TiO_2/m^3 for 7.25 hours. The test TiO_2 dust had an AMMD of 0.88 μM with a σg of 1.67. Immediately following the challenge, fifteen animals from each of the clean air control (CA), nonirradiated (NI) and irradiated (I) exhaust treatments were sacrificed with pentobarbital, and the lungs removed for titanium analysis. The remaining hamsters were returned to their respective treatment atmosphere. Additional subsets of 15 animals from each treatment (CA, NI, I) were sacrificed after 8 and 25 days of exposure. The lungs were weighed, lyopholized, wet ashed and assayed for Ti by a spectrophotometric method using 4,4-diantipyrylmethane monohydrate.[1] The results are expressed as μg Ti/gm lung dry weight and as percent of initial deposition.

RESULTS

Immediately following exposure to TiO_2, an average of 109.98 μg TiO_2 (65.99 μg Ti) was deposited in the lungs. This is equivalent to a pulmonary deposition of 15.4 ml of aerosol per minute which is in good agreement with values (11.0) estimated from the data of Ferin (1971).[1]

Table 1 shows the lung burden of titanium expressed as μg Ti/gm lung dry weight and as percent of initial deposition at 0, 8, and 25 days post TiO_2 challenge in hamsters exposed to clean air, nonirradiated and irradiated exhaust. No statistically significant treatment effects were observed when the data as μg Ti/gm lung were analyzed by analysis of variance. However, when the data for each treatment were normalized to percent of initial deposition, a significant increase (12.5%) in titanium clearance was noted on day eight. No effect was seen on day 25, possibly due to an unexplained larger variance in these groups. This pattern of behavior was noted in another study (Hall et al., unpublished)

Table 1

Pulmonary Clearance following Exposure to Catalytic-Treated Auto Exhaust: TiO_2 Challenge Lung Burden

Treatment	N/Cell	Lung Burden of Test Titanium µg/gm/(% initial deposition)		
		Day 0	Day 8	Day 24
CA	15	561.06 (100)	519.37 (92.61)	412.65 (73.55)
Nonirradiated Exhaust	15	588.50 (100)	532.42 (90.49)	392.81 (66.74)
Irradiated Exhaust	15	571.22 (100)	463.11 (80.99)*	401.40 (70.27)

*Significant at $p = .05$

DISCUSSION

Maintanence of the integrity of the pulmonary cleansing mechanisms is of paramount importance to the well-being of the organism. Changes in these parameters, such as increased sputum i.e. mucus production, are correlated with chronic obstructive lung disease.[2] Experimental induction of lung cancer in an animal model was considered a difficult task before the discovery of administering the chemical carcinogen carried by an inert dust.[3] Consequently, exposure to air pollutants which effect the pulmonary cleansing mechanism could have profound adverse effects on the well-being of the organism.

In this study, the efficiency of the lung cleansing mechanism was assessed by exposing the hamsters to a test dust with minimal biological activity and very low solubility. By comparison to clean air control animal deposition and clearance behavior, changes due to experimental treatment can be detected by difference in initial deposition (existent lung pathology or abnormal physiology) or changes in the rate and extent of removal of the challenge from the lungs of the auto exhaust exposed animals. Following continuous exposure to catalytic treated auto exhaust for seven days, no difference in initial TiO_2 deposition was found between the control and treatment groups. This would suggest minimal or no obstructive pulmonary pathology.

An accelerated removal of the inert dust was found in hamsters exposed to irradiated exhaust at eight days post challenge suggesting an increase in the rate of phagocytosis-mucociliary clearance mechanism. Twenty-five days after administration of TiO_2, no difference between the controls and treatment groups were detected. This was due to the large increase in variance in this time period. The significance of this phenomenon is not known. Likewise it is not possible from this experimental design to determine whether those parameters responsible for the eight day affect remained changed or returned to control rates. Further studies are necessary to ascertain any long term effects of the observed change in pulmonary clearance and its physiological significance.

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Appendix B6.1

Meteorological Modelling: Summary

An essential step between identification of an emission product and assessment of potential public health risk is the ability to estimate human exposures. For pollutants specific to the automobile, a highway air pollution model has been developed to predict stable, gaseous pollutant concentrations under various meterological conditions at the edge of and at substantial distances from a "simple" highway (Appendix B6.2) Exposure predictions specific to unique catalyst non-regulated emissions products (sulfuric acid aerosols and noble metal particulates) have been estimated utilizing this gaseous dispersion model. A contractural program with ESL, Incorporated (Contract no. 68-02-1233) was undertaken in June, 1973 to assess the applicability of this model under real-world conditions by measurement of a gaseous inert tracer (SF_6) released from a moving vehicle. A final report has not been received at this time.

The dispersion model discussed relates to distribution of a stable, gaseous emission product. The validity of the exposure estimates calculated using this model for acid aerosols or particulates is not quantatively known. In addition, application of such a model to complex vehicular sources or downtown street canyons is probably inappropriate. An expanded FY75/76 program has been planned to assess the validity of the gaseous dispersion model for estimating exposures to aerosols and particulates from moving vehicular sources. It is also intended that a complex source/street canyon dispersion model be developed.

The attached paper "Line Source Modeling" (B6.2) was recently prepared which discusses the Gaussian approach to modelling the line source in more detail than previously available and shows sensitivity of the model to several parameter changes. The paper uses the catalyst-sulfate issue as an example, and therefore expands upon the similar usage in EPA's earlier projections of sulfate exposures on and near major highways.

The ESL contract, discussed above, which utilizes SF_6 as a trace to validate the line source dispersion model, while not in final report form, suggests that the sigma parameters used are too small by a factor of two or three within 100m downwind of the highway. There are also indications that the Gaussian nature of dispersion closer than 20m to the highway should be questioned. A more extensive discussion of the sigma problem is found in the attached paper, "State-of-the-Art of Transportation Diffusion Calculations including Recommended Improvements" (B6.3).

EPA-650/4-74-008

Appendix B6.2

USER'S GUIDE FOR HIWAY, A HIGHWAY AIR POLLUTION MODEL

by

John R. Zimmerman
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Program Element 1AA009

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February 1975

USER'S GUIDE FOR HIWAY, A HIGHWAY AIR POLLUTION MODEL

I. INTRODUCTION

The National Environmental Policy Act of 1969 requires any Federally funded highway construction project to be preceded by an impact statement analyzing the effect of the proposed roadway on air quality. This report describes a computer program, called HIWAY, for calculating air quality levels of nonreactive pollutants produced by highway automotive traffic at distances of tens to hundreds of meters downwind of the highway in relatively uncomplicated terrain.

In making estimates of pollution concentrations for an "at-grade" highway, highway emissions are considered to be equivalent to a series of finite line sources. Each lane of traffic is modeled as though it were a straight, continuous, finite line source with a uniform emission rate. Air pollution concentrations downwind from a line source are found by a numerical integration along the line source of a simple Gaussian point-source plume. Although most applications of this model will be for ground-level sources and receptors, and for receptors close to the source where mixing height will have almost no effect, the more general case of nonzero source and receptor heights and inclusion of the effects of mixing height can be considered by the model.

The HIWAY model is similar to the line-source equations (5.19 and 5.20) in the *Workbook of Atmospheric Dispersion Estimates* (Turner, 1970) but can also consider finite line sources at any angle to the wind.

An estimate may also be made of air pollution concentrations downwind of a "cut section." To do this, the top of the cut section is considered to be equivalent to an area source. This area source is simulated by using a series of ten equal line sources such that the total source strength is equal to the total pollution emissions of the highway.

No pollution emissions module is included in the batch (card input) version of the model. A value of the line-source strength, q_ℓ (g m^{-1} sec^{-1}), for each lane of traffic must be obtained from a separate computation (Beaton et al., 1972). Line-source strength is generally a function of traffic rate, average vehicle speed, and traffic mix (fraction of heavy-duty vehicles, fraction of late models with emission control devices, etc.). Data input for the HIWAY program can be accomplished in two ways: (1) through batch mode, with data cards that follow the program deck (see Section 4 for format) and (2) through continuous mode, that is, interactively on a time-share computer terminal. The term interactive refers to the information exchange between the user and the computer program in asking and answering questions.

In the interactive version of the model, to be discussed in Section 4 and Appendix A, the user can obtain a crude estimate of line-source emission rate for the pollutant carbon monoxide. If one does not enter emission rates interactively, an estimate of emission rate can be determined by entering a value for vehicle speed and traffic volume per hour for each lane of traffic. This emission rate is representative of that for 1969 model-year automobiles (Ludwig et al., 1970). According to *Compilation of Air Pollutant Emission Factors* (EPA, 1973), this emission factor of 58.7 g veh^{-1} mi^{-1} for a speed of 19.6 mi hr^{-1} is also representative of emissions for the vehicle model mix near the end of 1973. See Table 3.1.1-1 in EPA, 1973.

2. DESCRIPTION OF MODEL

AT-GRADE HIGHWAY

A view of an idealized four-lane at-grade highway is shown in Figure 1. Traffic pollution emissions from each lane are simulated in the computer model by a straight line source of finite length. As shown in Figure 1 for a four-lane highway, the location of the highway is specified by the coordinates at the centerline (from edge to edge) of the highway (points 1 and 2). The ordering of the lanes is from left to right when one looks from point 1 to point 2. One lane or any even number of lanes from 2 to 24 can be used in the model.

The width of the highway and its center strip must also be entered as input data. With this information, the computer program HIWAY will assign a finite uniform line source to each lane of traffic. These line sources are placed at the center of each traffic lane.

A uniform emission rate, q_ℓ, must be specified for each line source. This line-source emission rate can be found if the emission factor, *EF* (g veh^{-1} mi^{-1}), and the traffic volume, *TV* (veh hr^{-1}), are known:

$$q_\ell\,(\mathrm{g\ sec^{-1}\ m^{-1}}) = \frac{EF\ (\mathrm{g\ veh^{-1}\ mi^{-1}})\ TV\ (\mathrm{veh\ hr^{-1}})}{1609.3(\mathrm{m\ mi^{-1}})\ 3600\ (\mathrm{sec\ hr^{-1}})} \tag{1}$$

$$= 1.726 \times 10^{-7}\ (EF)\ (TV)$$

A value of the emission factor for vehicles can be obtained from the most current issue of *Compilation of Air Pollutant Emission Factors* (EPA, 1973). It should be noted that for many pollutants the emission factor varies with vehicle speed.

Calculations

The calculation of concentration is made by a numerical integration of the Gaussian plume point-source equation over a finite length. The coordinates (meters) of the end points of a line source of length *D* (meters),

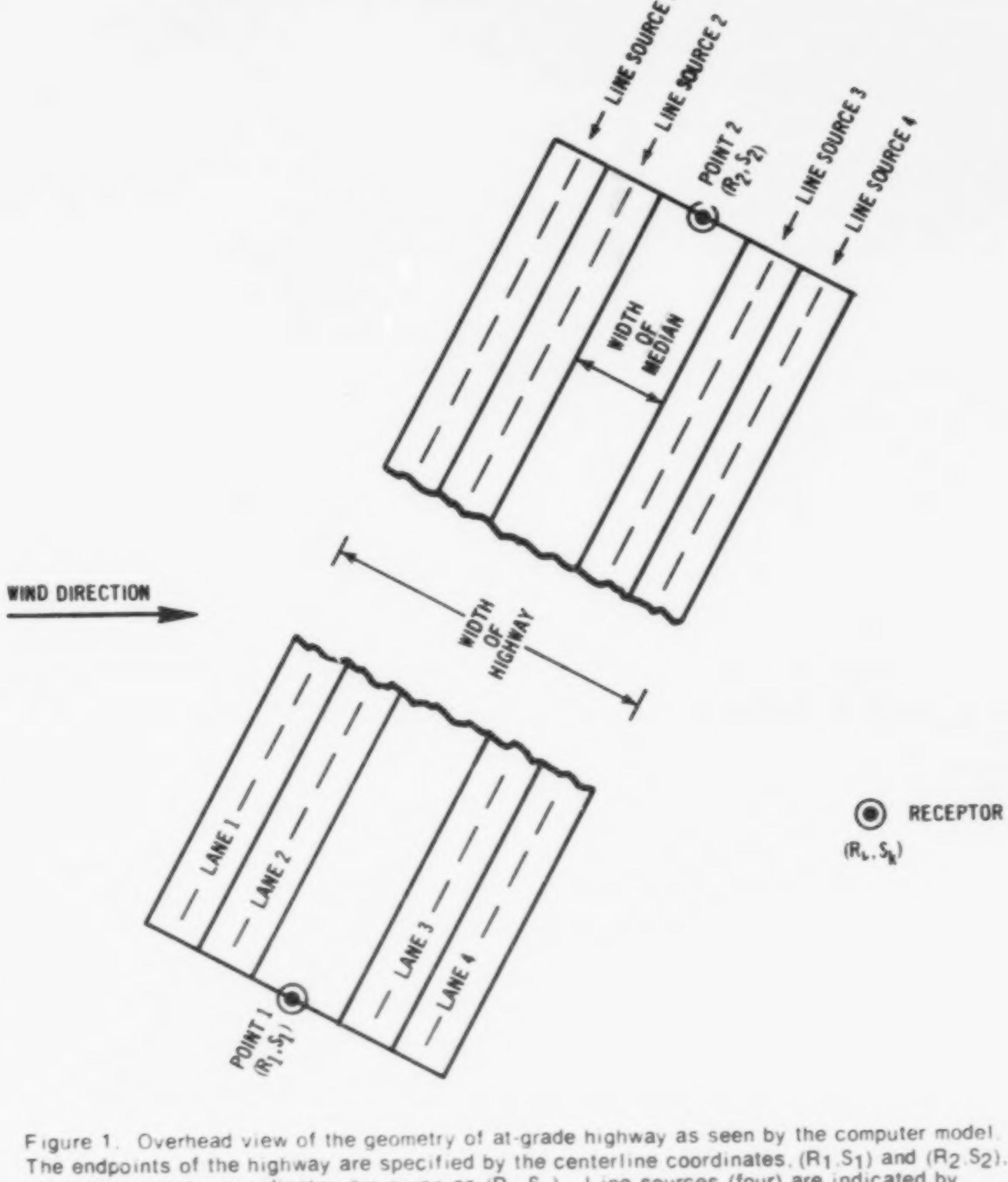
LINE SOURCE 1
LINE SOURCE 2
POINT 2 (R_2,S_2)
LINE SOURCE 3
LINE SOURCE 4
WIDTH OF MEDIAN
WIND DIRECTION
WIDTH OF HIGHWAY
LANE 1
LANE 2
LANE 3
LANE 4
POINT 1 (R_1,S_1)
RECEPTOR
(R_k,S_k)

Figure 1. Overhead view of the geometry of at-grade highway as seen by the computer model. The endpoints of the highway are specified by the centerline coordinates, (R_1,S_1) and (R_2,S_2), while the receptor coordinates are given as (R_k,S_k). Line sources (four) are indicated by the dashed lines at the center of each lane of traffic.

representing a single lane extending from point A to point B (see Figure 2), are R_A,S_A and R_B,S_B. The direction of the line source from A to B is β (degrees). The coordinates, R,S, of any point along the line at an arbitrary distance, ℓ (meters), from point A are given by:

$$R = R_A + \ell \sin\beta \tag{2}$$

$$S = S_A + \ell \cos\beta \tag{3}$$

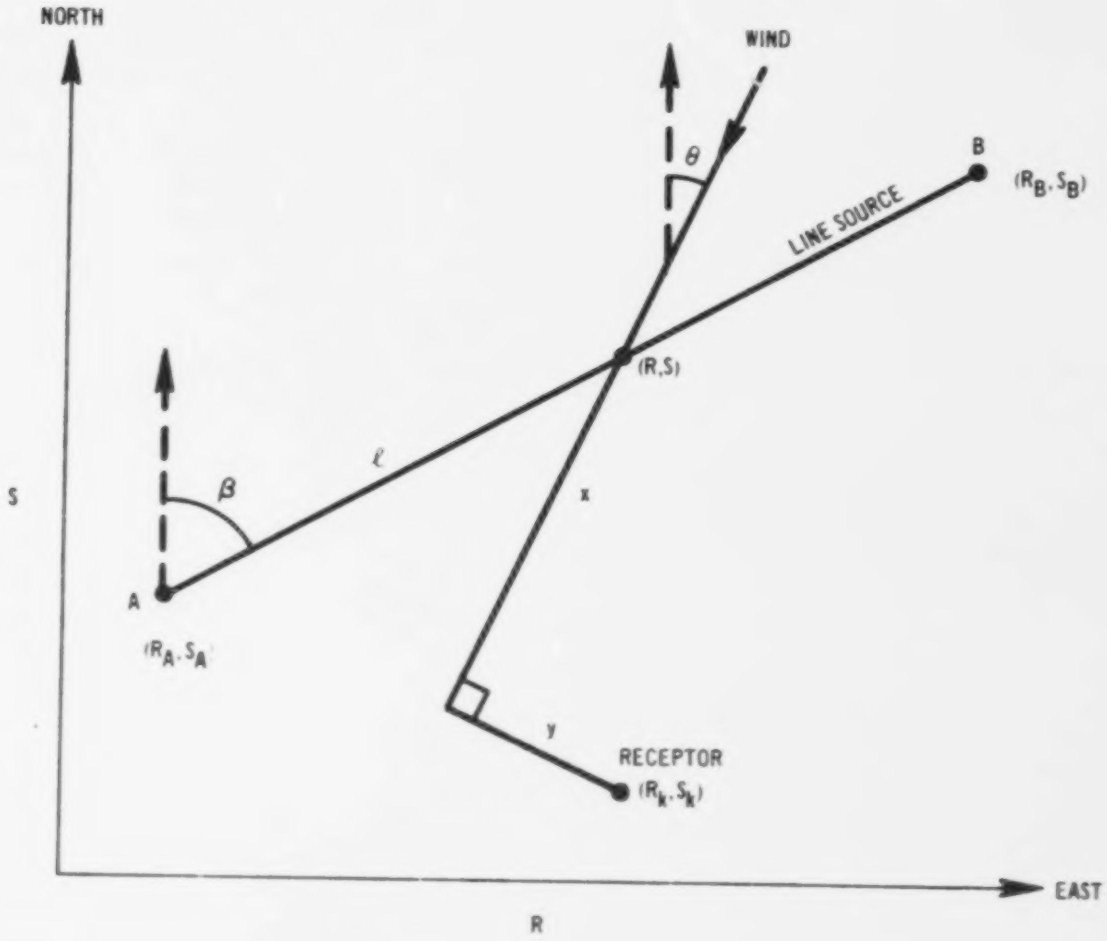
NORTH
WIND
θ
B
(R_B,S_B)
LINE SOURCE
(R,S)
ℓ
β
S
x
A
(R_A,S_A)
y
RECEPTOR
(R_k,S_k)
EAST
R

Figure 2. Line source and receptor relationships.

Given a receptor at R_k, S_k, the downwind distance, x (meters), and the crosswind distance, y (meters), of the receptor from the point R, S for any wind direction, θ (degrees), is given by:

$$x = (S - S_k)\cos\theta + (R - R_k)\sin\theta \tag{4}$$

$$y = (S - S_k)\sin\theta - (R - R_k)\cos\theta \tag{5}$$

Since R and S are functions of ℓ, x and y are also functions of ℓ. The concentration, χ (g m^{-3}), from the line source is then given by:

$$\chi = \frac{q_\ell}{u}\int_0^D f\,d_\ell \tag{6}$$

where:

u = wind speed, m sec^{-1}

D = line source length, meters

f = point source dispersion function (Equations 7 to 9), m^{-2}

For application of this model to a highway segment in relatively open terrain, an approximate estimate of the wind speed, u, at 2 meters height above ground is suitable.

For stable conditions or if the mixing height is $\geq$ 5000 meters,

$$f = \frac{1}{2\pi\sigma_y\sigma_z}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\left\{\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right]\right\} \tag{7}$$

where:

σ_y = standard deviation of the concentration distribution in the crosswind direction, meters

σ_z = standard deviation of the concentration distribution in the vertical direction, meters

z = receptor height above ground, meters

H = effective source height, meters

In unstable or neutral conditions, if σ_z is greater than 1.6 times the mixing height, L (meters), the distribution below the mixing height is uniform with height regardless of source or receptor height, provided both are less than the mixing height:

$$f = \frac{1}{\sqrt{2\pi}\sigma_y L} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \tag{8}$$

In all other unstable or neutral conditions:

$$\begin{aligned} f = \frac{1}{2\pi\sigma_y\sigma_z} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \Bigg\{ &\exp\left[-\frac{1}{2}\left(\frac{z-H}{\sigma_z}\right)^2\right] \\ &+ \exp\left[-\frac{1}{2}\left(\frac{z+H}{\sigma_z}\right)^2\right] + \sum_{N=1}^{N=\infty}\Bigg[\exp -\frac{1}{2}\left(\frac{z-H-2NL}{\sigma_z}\right)^2 \\ &+ \exp -\frac{1}{2}\left(\frac{z+H+2NL}{\sigma_z}\right)^2 + \exp -\frac{1}{2}\left(\frac{z-H+2NL}{\sigma_z}\right)^2 \\ &+ \exp -\frac{1}{2}\left(\frac{z+H+2NL}{\sigma_z}\right)^2\Bigg]\Bigg\} \end{aligned} \tag{9}$$

The infinite series in Equation 9 converges rapidly, and more than four or five sums of the four terms are seldom required.

In each of the three above equations, σ_y and σ_z are evaluated for the given stability class and the distances $x + b$ for σ_y and $x + a$ for σ_z. The virtual distances, a and b (km), are required to produce the initial σ_z and σ_y (σ_{zo} and σ_{yo}), respectively.

If z, H, or both are zero, the resulting simpler forms of Equations 7, 8, and 9 are used by the computer program.

The value of the integral in Equation 6 is approximated by use of the trapezoidal rule. Let $\Delta \ell = D/N$. Then the trapezoidal approximation gives:

$$\chi = \frac{q_\ell \, \Delta \ell}{u} \left[\frac{1}{2} (f_0 + f_N) + \sum_{i=1}^{N-1} f_i \right] \qquad (10)$$

where f_i is evaluated, as appropriate, from Equation 7, 8, or 9 for $\ell = i\Delta \ell$. The distances x and y are, of course, functions of ℓ.

For a given initial choice of the interval length, $\Delta \ell$, the calculation is then successively repeated with twice the number of intervals, that is, with $\Delta \ell/2$, $\Delta \ell/4$ ...., until the concentration estimates converge to within 2 percent of the previous estimate. This value is then used as the value of the integral.

The above evaluation of the integral is repeated for each lane of traffic, and the resulting concentrations are summed to represent the total concentration from the highway segment.

Computer Model

The FORTRAN computer program consists of a main program, three subroutines, and two functions. The main program handles input and sets up a separate line source for each lane of traffic. Subroutine DBTLNE does the integration and output of results. This subroutine calls DBTRCX, which evaluates Equations 7, 8, or 9, or simplifications of these equations if H or z is zero. Evaluation of σ_y and σ_z are done by subroutine DBTSIG, which is called from DBTRCX. Functions XVY and XVZ determine virtual distances for a given stability class corresponding to the initial σ_y and initial σ_z, respectively.

An east-north coordinate system is used in the computer model. The width of the highway and of its center strip, the coordinates of the centerline of the highway, and the coordinates of the receptor(s) are input parameters.

It should be noted that in Equations 4 and 5, x and y refer to a coordinate system aligned along the wind vector (x the downwind direction, and y the crosswind direction). That system is distinct from the coordinate system used for locating sources and receptors in the model.

In the basic equations given earlier (Equations 2 to 5), units of the coordinate system have been specified as meters for dimensional balance. However, units of the computer coordinate system, for practicality, are in kilometers. The user may use any convenient highway map unit if he enters an appropriate scaling factor to convert those units to kilometers. For example, if it is desired to use the units of meters for highway coordinates, the scale factor should be entered as 0.001. Section 4 contains a list of the input variables, including a brief description of each of the units by which the input parameters must be expressed. An example of input data, as well as the output of a run made with the example input data, is given in Appendix A.

CUT SECTION

Estimates of air pollution concentrations at locations downwind of a depressed highway (cut section) can be determined by considering the top of the cut section to be an area source of pollution (Figure 3). In the model, this area source is approximated by using ten line sources located at the top of the cut section. The total emission rate for the highway is first found by adding together the emission rates for each individual lane of traffic. Then this emission rate is distributed equally over each of the ten line sources used to simulate the area source at the top of the cut section.

Once this has been done, the procedure used to determine pollutant concentrations downwind of the cut section is entirely similar to the procedure used to determine the concentrations for an at-grade highway. It should be emphasized that these estimates of air pollution concentrations should be made for receptors downwind of the cut section and not for locations inside the cut section itself.

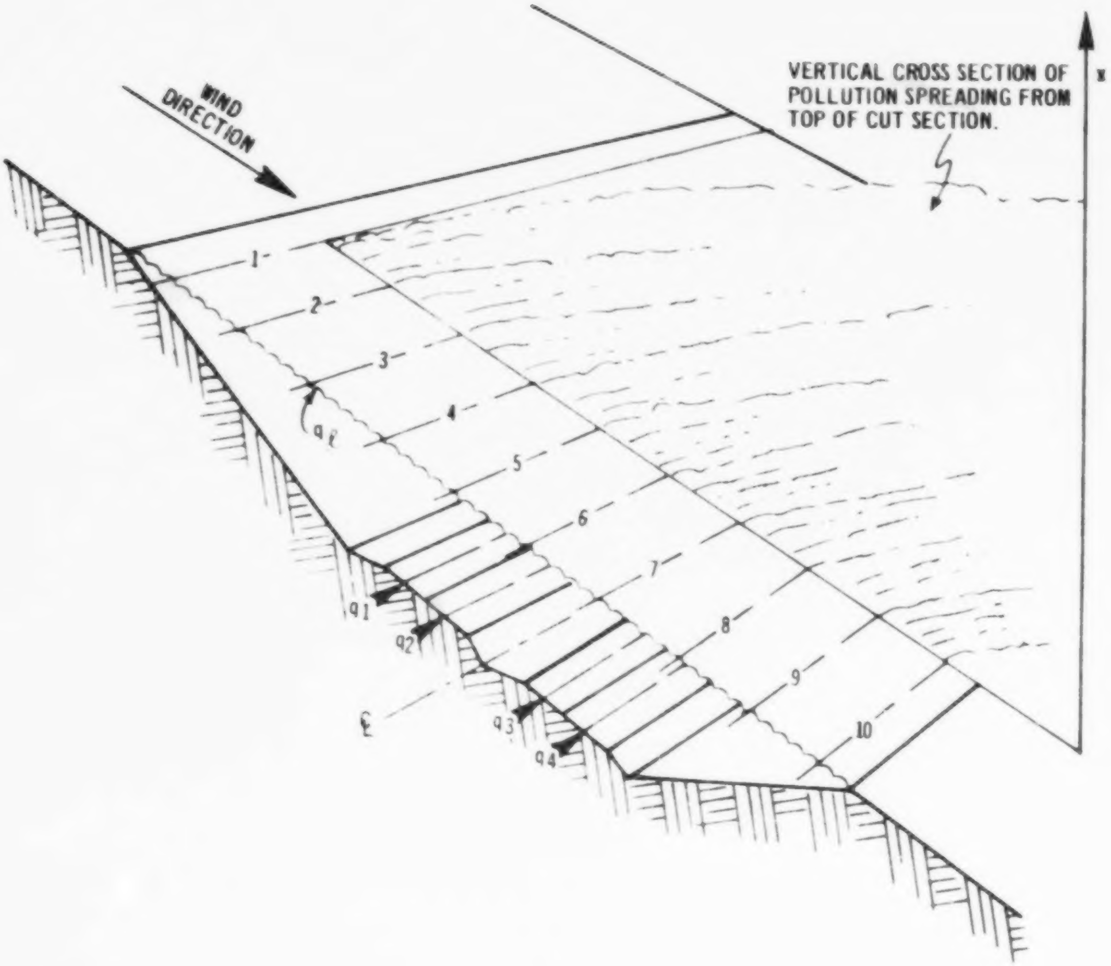
WIND DIRECTION
VERTICAL CROSS SECTION OF POLLUTION SPREADING FROM TOP OF CUT SECTION.
x
1
2
3
4
5
6
7
8
9
10
q_ℓ
q_1
q_2
q_3
q_4
℄

Figure 3. Method of simulating dispersion from a cut section. In this illustration, there are four lanes of traffic in a cut section with pollution emission rates q_1, q_2, q_3, and q_4. These emission rates are summed up and distributed equally over ten line sources placed at the top of the cut section, i.e., $q_\ell = (q_1 + q_2 + q_3 + q_4)/(10)$.

3. DISPERSION FUNCTIONS σ_y AND σ_z

The dispersion functions σ_y and σ_z (meters) indicate the amount the pollutant plume has spread (dispersed) after leaving its source. The values for these functions are those of Pasquill (if the virtual distance is taken as zero) as given in graphical form in Turner (1970). Pasquill stability classes are given in Table 1.

Table 1. PASQUILL STABILITY CLASSES

Stability class[a]	Description
A (1)	Very unstable
B (2)	Moderately unstable
C (3)	Slightly unstable
D (4)	Neutral
E (5)	Slightly stable
F (6)	Moderately stable

[a] The stability classes are commonly referred to by letter. For input to the computer program, the numbers in parentheses are used.

The horizontal dispersion parameter value is given by

$$\sigma_y = 465.1\ (x + b) \tan \theta_p \tag{11}$$

where:

x = downwind distance from source to receptor, km

b = virtual distance for initial σ_y, km

θ_p = half angle of horizontal plume spreading, degrees

The factor 465.1 is 1000 m km^{-1} divided by 2.15, the number of standard deviations of a Gaussian distribution from the centerline to the point where the distribution falls to 10 percent of the centerline value. The angle θ_p is given by:

$$\theta_p = c - d \ln\left(\frac{x + b}{x_0}\right) \tag{12}$$

where c and d (degrees) are functions of Pasquill stability class and the normalizing distance, x_o, is 1 km. Values of the parameters c and d are given in Table 2.

Table 2. VALUES OF c AND d USED TO CALCULATE θ_p

Stability class	Value, degrees	
	c	d
A (1)	24.167	2.5334
B (2)	18.333	1.8096
C (3)	12.5	1.0857
D (4)	8.333	0.72382
E (5)	6.25	0.54287
F (6)	4.167	0.36191

The vertical dispersion parameter value, σ_z (meters), is given by equations of the form:

$$\sigma_z = g\left(\frac{x + a}{x_o}\right)^h \tag{13}$$

where a is the virtual distance (km) to give the initial σ_z (meters), and g (meters) and h (dimensionless) are functions of stability class and also various ranges of the distance x. When a is zero, the values are the same as those in Figure 3-3 of Turner (1970). Since the values of σ_z for x less than 0.1 km are not given in that figure, the values of the parameters g and h for x less than 0.1 km are given in Table 3. The values corresponding to g and h for x at other distances can be determined by examining the program listing for subroutine DBTSIG (Appendix B).

Turbulence of the air produced by the motion of automobiles results in a rapid mixing of the pollutants near the highway. This is modeled by assuming that an initial spreading of the pollutant plume occurs over the highway. To determine an acceptable initial vertical plume spread, data taken near at-grade sections from various highways were used. When the

Table 3. VALUES OF *g* AND *h* USED TO DETERMINE σ_z FOR DOWNWIND DISTANCES LESS THAN 0.1 km

Stability class	Value	
	g, meters	*h*, dimensionless
A (1)	122.8	0.9447
B (2)	90.673	0.93198
C (3)	61.141	0.91465
D (4)	34.459	0.86974
E (5)	24.26	0.8366
F (6)	15.209	0.81558

wind direction is less than 75 degrees from the perpendicular to the highway, it has been shown that an approximate expression can be used to determine pollutant concentrations from an infinite line source (Calder, 1973). Solving this expression for σ_z yields:

$$\sigma_z(x) = \sqrt{\frac{2}{\pi}} \quad \frac{q_\ell}{C(p)\ u \cos\gamma} \tag{14}$$

where:

$\sigma_z(x)$ = the vertical standard deviation of plume distribution at the downwind distance, x, from the source

$C(p)$ = the measured concentrations at the perpendicular distance, p (meters), from the highway $\left(x = \frac{p}{\cos\gamma}\right)$, g m^{-3}

γ = the angle between the wind direction and a perpendicular to the highway, degrees

By making estimates of the line-source emission rate, q_ℓ, and obtaining observed data for air pollution concentrations, a plot of σ_z versus distance was determined (Figure 4). From this analysis, it is seen that an initial σ_z (σ_{zo}) equal to 1.5 meters is a conservative approximation of the vertical

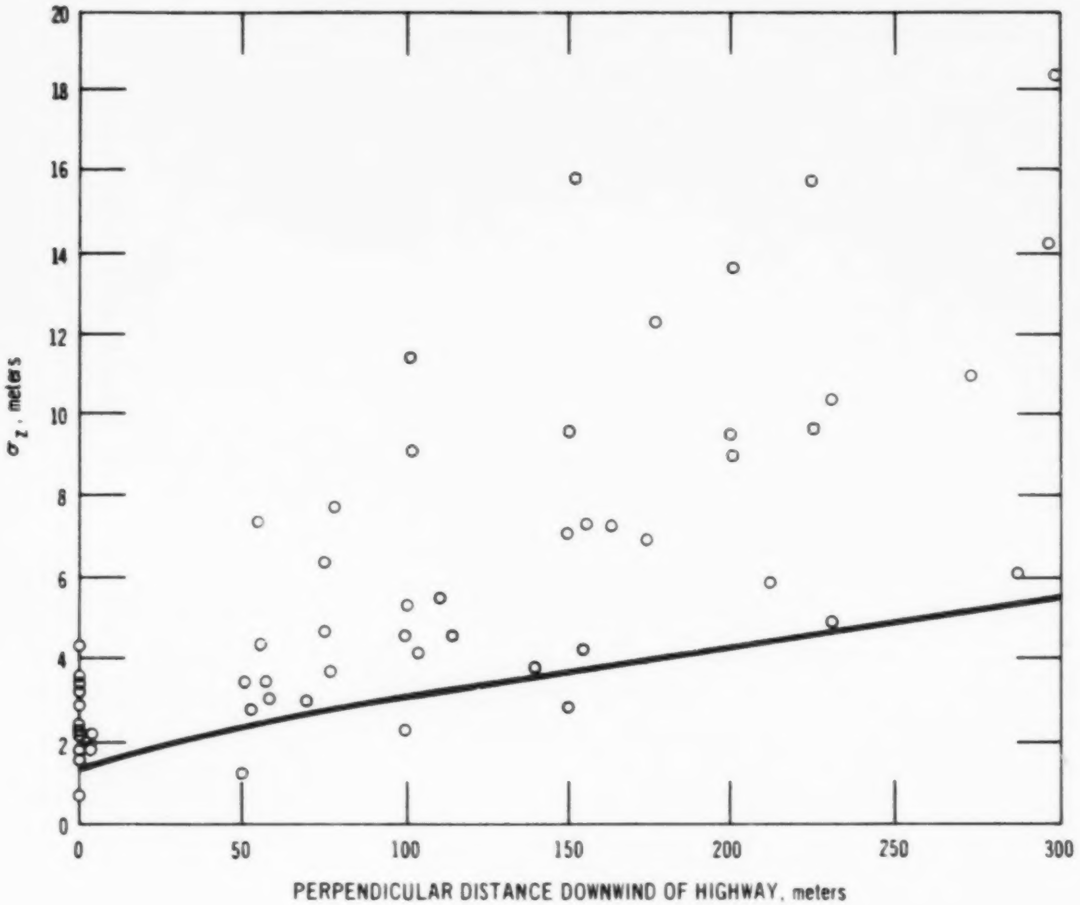

Figure 4. Data points used to determine an estimate of initial σ_z. Also plotted is the $\sigma_z(x)$ curve for neutral stability. The line is the approximate lower bound of the data.

standard deviation of the plume at the downwind edge of the at-grade highway. This is only a tentative value based on a limited amount of data and may be revised as more data become available. This empirical value of σ_{zo} is applied in the operation of the model to each of the line sources placed along each lane of traffic.

For at-grade pollution dispersion, an arbitrary value for initial σ_y (σ_{yo}) of 3 meters (approximately one-half the length of a car) was selected. The value given to σ_{yo} has little effect on the computation of air pollution concentrations when the wind direction has a component perpendicular to the highway. The use of an initial σ_y is to account for a reasonable amount of cross-highway spreading caused by vehicle-generated turbulence when the wind direction is parallel or nearly parallel to the highway.

The virtual distances, a, corresponding to an initial σ_z of 1.5 meters and the virtual distances, b, corresponding to an initial σ_y of 3.0 meters for each stability class are given in Table 4.

Table 4. VIRTUAL DISTANCES a AND b CORRESPONDING TO INITIAL σ_z OF 1.5 METERS AND INITIAL σ_y OF 3.0 METERS, RESPECTIVELY

Stability class	Distance, km	
	a	b
A (1)	0.00944	0.00863
B (2)	0.01226	0.0132
C (3)	0.01736	0.0210
D (4)	0.02722	0.0348
E (5)	0.03590	0.0471
F (6)	0.05842	0.0733

There are very few published measurements of air quality downwind of a cut section. Nevertheless, the available data indicate that the cut-section configuration tends to increase the dispersion of the air pollution originating from the cut section. This is particularly true when wind speeds are light, for then the release of heat from combustion, the long travel time of the pollutant to the receptor, and mechanical turbulence produced by the cut-section highway aid the dispersion. Thus, for the cut-section case, based upon very limited data, the initial σ's for wind speeds less than 1 m sec^{-1} were set at 10 meters for σ_y and 5 meters for σ_z. It was assumed that for wind speeds greater than 3 m sec^{-1} the cut section did not enhance the initial dispersion and that it was the same as for the at-grade highway: 3 meters for σ_y and 1.5 meters for σ_z. For speeds between 1 and 3 m sec^{-1}, the initial sigmas are linearly interpolated. These initial σ's are assumed for each of the ten lanes used to represent the cut. The initial values of σ_y and σ_z (meters) are found from:

$$\left.\begin{array}{l}\sigma_{yo} = 3 \\ \\ \sigma_{zo} = 1.5\end{array}\right\} \text{ for } u > 3 \text{ m sec}^{-1} \tag{15}$$

$$\left.\begin{array}{l}\sigma_{yo} = 10 - 7\left(\dfrac{u - 1}{2}\right) \\ \\ \sigma_{zo} = 5 - 3.5\left(\dfrac{u - 1}{2}\right)\end{array}\right\} \text{ for } 1 < u < 3 \text{ m sec}^{-1} \tag{16}$$

and

$$\left.\begin{array}{l}\sigma_{yo} = 10 \\ \\ \sigma_{zo} = 5\end{array}\right\} \text{ for } u < 1 \text{ m sec}^{-1} \tag{17}$$

4. PREPARATION OF INPUT DATA

CARD INPUT SEQUENCE

The arrangement of data on the input cards for the batch mode of operation is given in Table 5. The coordinates of the roadway are in the center of the highway (from edge to edge). The ordering of the lanes is from left to right when looking from point 1 to point 2.

INTERACTIVE OPERATION

The HIWAY model has been placed on the Environmental Protection Agency's (EPA) Users' Network for Applied Modeling of Air Pollution (UNAMAP) computer system and is accessible to EPA users. The model is also on the UNAMAP system available to all users. For information on this system contact: Chief, Data Management, Meteorology Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, N. C. 27711.

The self-explanatory listing produced by the model on a remote computer terminal is shown in Appendix A to illustrate the operation of the model in an interactive mode. The computer communicates to the user in upper case letters, while the user replies in lower case letters. To initiate the program, the user issues the command, *hiway*.

Operation of the model in an interactive mode is similar to batch mode operation. To determine emission rates for the pollutant carbon monoxide, however, the user can elect the option to use the internally generated emission rates for carbon monoxide that are representative of the emissions for the vehicle model mix near the end of 1973. This applies a correction factor for vehicle speed.

Table 5. INPUT DATA CARDS

Name	Columns	Format	Form	Variable	Units
Card type 1 (1 card)					
Head	1-80	20A4	AAAA	Alphanumeric data for heading	-
Card type 2 (1 card)					
REP1	1-10	F10.0	XXXX.XXX	East coordinate, point 1	Map units
SEP1	11-20	F10.0	XXXX.XXX	North coordinate, point 1	Map units
REP2	21-30	F10.0	XXXX.XXX	East coordinate, point 2	Map units
SEP2	31-40	F10.0	XXXX.XXX	North coordinate, point 2	Map units
H	41-50	F10.0	XX.X	Height of line source	Meters
WIDTH	51-60	F10.0	XX.	Total width of highway	Meters
CNTR	61-70	F10.0	XX.	Width of center strip	Meters
XNL	71-80	F10.0	X.	Number of traffic lanes	-
Card type 3 (up to 3 cards)					
QLS	1-80	F10.0	.XXXXXXXXX	Emission rate for each lane	g $sec^{-1}m^{-1}$
Card type 4 (1 card, can be blank for at grade)					
CUT	1-10	F10.0	X.	1, if cut; 0, if at grade	-
WIDTC	11-20	F10.0	XX.	Width of top of cut section	Meters
Card type 5 (1 card)					
THETA	1-10	F10.0	XXX.	Wind direction	Degrees
U	11-20	F10.0	XX.X	Wind speed	m sec^{-1}
HL	21-30	F10.0	XXXX.	Height of mixing layer	Meters
XKST	31-40	F10.0	X.	Pasquill stability class	-
Card type 6 (1 card)					
GS	1-10	F10.0	X.	Scale factor[a]	-
Card type 7 (any number of cards)					
XXRR	1-10	F10.0	XXXX.XXX	East coordinate of receptor[b]	Map units
XXSR	11-20	F10.0	XXXX.XXX	North coordinate of receptor	Map units
Z	21-30	F10.0	XX.	Height (above ground) of receptor	Meters

[a] The scale factor converts map units to kilometers.
If map units in kilometers, scale factor = 1.0
If map units in meters, scale factor = 0.001
If map units in feet, scale factor = 0.000305
If map units in miles, scale factor = 1.61

[b] To begin again with another set of data, a value of 9999. is punched for XXRR (card type 7) following the last receptor card.

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GLOSSARY

Several frequently used terms have become part of the jargon used by air quality dispersion modelers, and these terms are defined briefly in this section. For a more complete discussion of the concepts implied by these terms, the reader should consult the references cited.

Stability class. Atmospheric stability ranked according to classes, which are given in indexes *A* through *F* (or 1 through 6), as shown in Table 1 (Pasquill, 1961). Class *A* is very unstable and is found when skies are clear and sunny, while class *F* is moderately stable and occurs under calm conditions on clear nights.

Mixing height. The height to which pollutants are actively mixed. The air close to the earth's surface generally becomes unstable after sunrise, resulting in a zone of vigorous atmospheric mixing in the layer of air at ground level. The height of this layer increases after sunrise and reaches a maximum about 4:00 p.m. (Holzworth, 1972). For most locations close to the pollution source, the mixing height will have very little influence on the calculation of pollution concentration. When the receptor is located at a great distance from the pollution source and the travel time of the pollutant from source to receptor location is long, the mixing height will be the limiting height to which pollution will spread vertically.

Receptor. A location for which it is desired to predict pollutant concentrations. When a model is being validated, it is necessary to obtain model predictions at the receptor locations for which air quality data are measured.

Emission rate of a line source. An estimate of the amount of pollution being generated by a line source (e.g., lane of automobile traffic). To determine this value, two pieces of information are required: (1) the volume of traffic and (2) the emission factor, which is dependent on vehicle speed. The emission rate can then be determined by

$$q_i = (CV)\,(EF)\,(TV)$$

where:

q_L = line source emission rate, g sec^{-1} m^{-1}
EF = emission factor, g veh^{-1} mi^{-1}
TV = traffic volume, veh hr^{-1}
CV = conversion constant = 1.726×10^{-7}, mi hr m^{-1} sec^{-1}

σ_y *and* σ_z: The standard deviation of concentration distribution in the horizontal and vertical planes, respectively. The values of σ_y and σ_z will increase with downwind distance from the source of pollution as the dimensions of the pollution plume increase. This increase in pollution plume dimension is caused by atmospheric turbulence. The intensity of atmospheric turbulence is in turn related to atmospheric stability. The plume growth will be greatest in an unstable atmosphere (more turbulence) and least when the atmosphere is stable.

APPENDIX A. EXAMPLE PROBLEM

INTRODUCTION

In order to clarify the procedure for using both the batch and interactive (continuous) versions of the HIWAY model, the following test problem is solved using both versions.

Given: Length of highway = 5 km.
Orientation = east-west.
Number of lanes = four.
Road width (edge to edge) = 46 meters.
Median width = 30 meters.
Emission rate in each lane from south to north = 0.0112, 0.0103, 0.0106, and 0.0156 g sec^{-1} m^{-1}.
Wind direction = 42 degrees.
Wind speed = 3.7 m sec^{-1}.
Stability class = 3.

Find: The expected concentration at receptors along a line perpendicular to the center of the highway segment at distances 1, 5, 10, 30, and 50 meters from the downwind edge of the roadway (1) if the road is an at-grade section, and (2) if the road is a cut section with the top of the cut being 50 meters in width.

SOLUTION USING THE INTERACTIVE VERSION

Assuming that you have already logged on the computer, etc., type in the name *hiway* as indicated in Table A-1. You are then given the choice of receiving a description of the model. Following that, enter the input parameters as the model calls for them. Most of them are self-explanatory; however, a few comments are in order:

1. When entering the mixing height never use the value 0.
2. If you do not want the effect of a limit to vertical mixing in your calculation, use a large enough mixing height so that there is no chance of its influencing your results, such as 5000 meters.

3. When entering the receptor coordinates, remember that this program is valid only downwind of the line source. A receptor location defined on the line source will not give a valid answer. If you are interested in the concentration at the edge of the highway, use a downwind distance greater than 0.1 meter from the edge of the highway and the result will be valid.

4. The coordinates for the ends of the roadway segment are assumed to be in the center of the road (from edge to edge).

5. The ordering of emission rates is for lanes in order from left to right when looking from point 1 to point 2.

The results for the at grade section are given following the entry of receptor coordinates. For convenience, the center of the roadway has been placed 0.023 km north of the origin in this example so that the edge of the road is on the axis and the y coordinate of the receptor is the distance from the edge of the road. The roadway and receptors could have been placed at any location.

The option to run the model for a new receptor location (LOC), change the road type (TYPE), or to end the program (END) is given after the results.

In the second part of the problem, the road type (cut), the width (50 meters), and the location of the road (to again place the edge of the road at a y coordinate value of zero) are changed. The results for the cut section are shown following the entry of data. Note that the concentrations are in micrograms per cubic meter (UGM/M**3). The part per million (PPM) column is a conversion from micrograms per cubic meter for the pollutant carbon monoxide. The part per million column would be incorrect for any other pollutant.

If you decide to continue and change the receptor locations (LOC), remember that the receptors must remain downwind from the downwind edge of the roadway.

SOLUTION USING THE BATCH VERSION

The batch version requires at least seven input cards. Depending upon the number of receptor points and number of problems to be run, there may be more. The format for each card is given in Table 5. Table A-2 lists the input for the example problem; Table A-3 lists the results. Note that for the cut section the sixth and seventh fields (columns 51 to 70) in card type 2 were left blank. Also note that the card with 9999. for the variable **XXRR** is only used if more than one set of input data are used. A card like this does *not* follow the last set of input data. As in the interactive version, the parts per million column is only valid if carbon monoxide is the pollutant being modeled.

Table A-1. EXAMPLE OF INTERACTIVE VERSION OF HIWAY

```
hiway

DO YOU WANT A DESCRIPTION OF THE EPA "HIWAY" MODEL
BEFORE APPLYING IT?(YES OR NO)

yes

1.THE EPA "HIWAY" MODEL COMPUTES INERT POLLUTANT CONCENTRATIONS IN THE
  VICINITY OF A ROADWAY ON A SHORT TERM BASIS (HOURLY AVERAGES) USING
  THE GAUSSIAN PLUME FORMULATION. IF MORE THAN ONE ROADWAY IS PRESENT,
  SUPERPOSITION APPLIES. THE MODEL CAN BE USED FOR AT GRADE AND CUT
  SECTIONS FOR RECEPTOR DISTANCES OF TENS TO HUNDREDS OF METERS DOWNWIND
  OF THE LINE SOURCE IN RELATIVELY UNCOMPLICATED TERRAIN.
2.THE COORDINATE SYSTEM IS ARRANGED SUCH THAT THE X-AXIS INCREASES FROM
  WEST TO EAST WHILE THE Y-AXIS INCREASES FROM SOUTH TO NORTH.THE UNITS
  RELATED TO HIGHWAY MEASUREMENTS ARE INDICATED BY A SCALE FACTOR OF
  USER UNITS TO KILOMETERS. THE MOST FREQUENTLY USED FACTORS ARE:
                  UNITS               SCALE FACTOR
                 KILOMETERS            1.0
                 METERS                0.001
                 FEET                  0.000305
                 MILES                 1.61
  SCALE FACTOR UNITS APPLY EXCEPT WHEN OTHER UNITS ARE SPECIFICALLY
  REQUESTED.
3.THE EMISSION DATA IS DEPENDENT ON VEHICLE SPEED,TYPES AND NUMBER OF
  VEHICLES,AND EMISSION CONTROL DEVICES.THE PROGRAM WILL GENERATE AN
  EMISSION RATE BASED ON AN ESTIMATE OF AVERAGE ROADWAY SPEED AND
  VOLUME OF TRAFFIC.ALTERNATIVELY,THE USER CAN ELECT TO SPECIFY HIS
  OWN EMISSION RATES IN GRAMS PER SECOND-METER.THE LATTER APPROACH IS
  HIGHLY PREFERABLE SINCE THE INTERNALLY GENERATED RATE IS BASED UPON
  A SPECIFIC AUTOMOBLE MIX (END OF 1973) WHICH DOES NOT APPLY ACCURATELY
  IN MOST CASES.  EMISSIONS (GM/SEC•M) ARE ENTERED IN ORDER FROM LEFT
  TO RIGHT WHEN LOOKING FROM ROAD END PT 1 TO END PT 2.
4.ROAD COORDINATES ARE THE ENDPOINTS OF THE HIGHWAY CENTER LINE.
  WIND DIRECTION IS DERIVED BY MEASURING CLOCKWISE(EAST) FROM
  DUE NORTH.(E.G.,WIND FROM NORTH IS 0 DEGREES;EASTERLY WIND IS 90.)
5.THE PROGRAM CONTAINS THE OPTION TO EVALUATE ANY NUMBER OF
  RECEPTOR LOCATIONS AND/OR TYPES OF ROADS.
6.YOU MUST SEPARATE MULTIPLE INPUTS WITH COMMAS.
7.FOR MOST APPLICATIONS,THE HEIGHTS OF THE RECEPTOR AND
  SOURCES ARE ASSUMED TO BE THE SAME.
```

Table A-1 (continued). EXAMPLE OF INTERACTIVE VERSION OF HIWAY

```
 DO YOU WANT A DESCRIPTION OF THIS VERSION OF "HIWAY"?(YES OR NO)
no
 ENTER SCALE FACTOR (USER UNITS/KILOMETER).
1
 ENTER LINE(ROAD) ENDPOINTS.(ORDERED PAIRS:X1,Y1,X2,Y2)
2.5,.023,-2.5,.023
 ENTER EMISSION HEIGHT. (METERS)
0
 ENTER WIND DIRECTION (DEG).  NORTH IS ZERO.
42
 ENTER WIND SPEED (METERS/SEC).
3.7
 ENTER MIXING HEIGHT (METERS).
1000
 ENTER PASQUILL-TURNER STABILITY CLASS (1-6).
3
 ENTER THE NUMBER OF LANES.
4
 DO YOU WISH TO ENTER YOUR OWN EMISSION RATES?(YES OR NO)
yes
 ENTER LINE SOURCE STRENGTH VECTOR.(A VALUE FOR EACH LANE)
.0112,.0103,.0106,.0156
 IS THIS A CUT SECTION?  (YES OR NO)
no
 ENTER HIWAY WIDTH (METERS).
46
 ENTER WIDTH OF CENTER STRIP (METERS).
30
 ENTER NUMBER OF RECEPTOR LOCATIONS DESIRED.(MAXIMUM OF 25)
5
 ENTER RECEPTOR COORDINATE SETS.(X&Y IN SCALE FACTOR UNITS;Z IN METERS)
0,-.001,0,0,-.005,0,0,-.010,0
0,-.030,0,0,-.050,0
```

Table A-1 (continued). EXAMPLE OF INTERACTIVE VERSION OF HIWAY

```
HIWAY VERSION: 74250
ENDPOINTS OF THE LINE SOURCE
    2.500,      .023  AND   -2.500,      .023
EMISSION HEIGHT IS    0.000 METERS
EMISSION RATE (GRAMS/SECOND*METER) OF    4 LANE(S)
    .112-01      .103-01      .106-01      .156-01
WIDTH OF AT-GRADE HIGHWAY IS    46.000 METERS
WIDTH OF CENTER STRIP IS    30.000 METERS
WIND DIRECTION IS    42.  DEGREES
WIND SPEED IS    3.7 METERS/SEC
STABILITY CLASS IS    3
HEIGHT OF LIMITING LID IS  1000.0 METERS
THE SCALE FACTOR IS     1.0000 USER UNITS/KM.


    RECEPTOR LOCATION        HEIGHT              CONCENTRATION
    X              Y         Z (M)        UGM/M**3      PPM*
    .0000        -.0010       .0000        4449.       3.871
    .0000        -.0050       .0000        3831.       3.333
    .0000        -.0100       .0000        3294.       2.866
    .0000        -.0300       .0000        2184.       1.900
    .0000        -.0500       .0000        1669.       1.452

* PPM CONCENTRATIONS CORRECT FOR CARBON MONOXIDE ONLY.
```

Table A-1 (continued). EXAMPLE OF INTERACTIVE VERSION OF HIWAY

```
 YOU HAVE THE OPTION TO RUN THE MODEL FOR A NEW RECEPTOR LOCATION
 (LOC),OR TO CHANGE THE ROADWAY TYPE,OR TO END THE PROGRAM.
 ENTER LOC, OR TYPE, OR END.
type
 ENTER LINE(ROAD) ENDPOINTS.(ORDERED PAIRS:X1,Y1,X2,Y2)
2.5,.025,-2.5,.025
 ENTER EMISSION HEIGHT. (METERS)
0
 ENTER WIND DIRECTION (DEG).  NORTH IS ZERO.
42
 ENTER WIND SPEED (METERS/SEC).
3.7
 ENTER MIXING HEIGHT (METERS).
1000
 ENTER PASQUILL-TURNER STABILITY CLASS (1-6).
3
 ENTER THE NUMBER OF LANES.
4
 DO YOU WISH TO ENTER YOUR OWN EMISSION RATES?(YES OR NO)
yes
 ENTER LINE SOURCE STRENGTH VECTOR.(A VALUE FOR EACH LANE)
.0112,.0103,.0106,.0156
 IS THIS A CUT SECTION?  (YES OR NO)
yes
 ENTER WIDTH OF TOP OF CUT. (METERS)
50
 ENTER NUMBER OF RECEPTOR LOCATIONS DESIRED.(MAXIMUM OF 25)
5
 ENTER RECEPTOR COORDINATE SETS.(X&Y IN SCALE FACTOR UNITS;Z IN METERS)
0,-.001,0,0,-.005,0
0,-.010,0,0,-.030,0
0,-.050,0
```

Table A-1 (continued). EXAMPLE OF INTERACTIVE VERSION OF HIWAY

```
HIWAY VERSION: 74250
ENDPOINTS OF THE LINE SOURCE
    2.500,      .025  AND   -2.500,      .025
EMISSION HEIGHT IS     .000 METERS
EMISSION RATE (GRAMS/SECOND*METER) OF    4 LANE(S)
    .112-01      .103-01      .106-01      .156-01
WIDTH OF TOP OF CUT SECTION IS     50.000 METERS
WIND DIRECTION IS     42.  DEGREES
WIND SPEED IS     3.7 METERS/SEC
STABILITY CLASS IS     3
HEIGHT OF LIMITING LID IS  1000.0 METERS
THE SCALE FACTOR IS      1.0000 USER UNITS/KM.


      RECEPTOR LOCATION        HEIGHT              CONCENTRATION
       X            Y          Z (M)      UGM/M**3      PPM*
      .0000       -.0010       .0000        3894.      3.388
      .0000       -.0050       .0000        3452.      3.003
      .0000       -.0100       .0000        3040.      2.645
      .0000       -.0300       .0000        2107.      1.833
      .0000       -.0500       .0000        1636.      1.423

* PPM CONCENTRATIONS CORRECT FOR CARBON MONOXIDE ONLY.



 ENTER LOC, OR TYPE, OR END.
end
```

Table A-2. CARD INPUT FOR EXAMPLE PROBLEM

```
         1         2         3         4         5         6         7         8
12345678901234567890123456789012345678901234567890123456789012345678901234567890
--------------------------------------------------------------------------------
    AT-GRADE SECTION     EXAMPLE FOR HIWAY USERS MANUEL
       2.5      .023      -2.5      .023        .0      46.0      30.0         4
     .0112     .0103     .0106     .0156
         0
        42       3.7      1000         3
         1
        .0     -.001        .0
        .0     -.005        .0
        .0     -.010        .0
        .0     -.030        .0
        .0     -.050        .0
     9999.
    CUT-SECTION          EXAMPLE FOR HIWAY USERS MANUEL
       2.5      .025      -2.5      .025        .0                             4
     .0112     .0103     .0106     .0156
         1        50
        42       3.7      1000         3
         1
        .0     -.001        .0
        .0     -.005        .0
        .0     -.010        .0
        .0     -.030        .0
        .0     -.050        .0
--------------------------------------------------------------------------------
12345678901234567890123456789012345678901234567890123456789012345678901234567890
         1         2         3         4         5         6         7         8
```

Table A-3. EXAMPLE OF BATCH VERSION OF HIGHWAY

```
@XQT HIWAYBATCH.KZ

   AT-GRADE SECTION     EXAMPLE FOR HIWAY USERS MANUEL

   HIWAY VERSION: 74250
 ENDPOINTS OF THE LINE SOURCE
   2.500,      .023 AND   -2.500,      .023
 EMISSION HEIGHT IS    .000 METERS
 EMISSION RATE (GRAMS/SECOND*METER) OF    4 LANE(S)
     .112-01     .103-01      .106-01      .156-01
 WIDTH OF AT-GRADE HIGHWAY IS       46.0 M
 WIDTH OF CENTER STRIP IS       30.0 M
 WIND DIRECTION IS     42.  DEGREES
 WIND SPEED IS     3.7 METERS/SEC
 STABILITY CLASS IS    3
 HEIGHT OF LIMITING LID IS  1000.0 METERS
 THE SCALE OF THE COORDINATE AXES IS     1.0000 USER UNITS/KM.


   RECEPTOR LOCATION        HEIGHT     CONCENTRATION
      X            Y           Z(M)    UGM/METER**3     PPM *
     .0000       -.0010       .0000        4449.       3.671
     .0000       -.0050       .0000        3831.       3.333
     .0000       -.0100       .0000        3294.       2.866
     .0000       -.0300       .0000        2184.       1.900
     .0000       -.0500       .0000        1669.       1.452

 *  PPM CONCENTRATIONS CORRECT FOR CARBON MONOXIDE ONLY.
```

Table A-3 (continued). EXAMPLE OF BATCH VERSION OF HIGHWAY

```
CUT-SECTION          EXAMPLE FOR HIWAY USERS MANUEL

  HIWAY VERSION: 74250
 ENDPOINTS OF THE LINE SOURCE
    2.500,     .025 AND   -2.500,      .025
 EMISSION HEIGHT IS    .000 METERS
 EMISSION RATE (GRAMS/SECOND*METER) OF    4 LANE(S)
     .112-01     .103-01     .106-01     .156-01
 WIDTH OF TOP OF CUT SECTION IS    50.000 M
 WIND DIRECTION IS    42.  DEGREES
 WIND SPEED IS    3.7 METERS/SEC
 STABILITY CLASS IS    3
 HEIGHT OF LIMITING LID IS  1000.0 METERS


 THE SCALE OF THE COORDINATE AXES IS     1.0000 USER UNITS/KM.


  RECEPTOR LOCATION        HEIGHT     CONCENTRATION
     X          Y            Z(M)     UGM/METER**3     PPM *
    .0000     -.0010        .0000        3894.         3.388
    .0000     -.0050        .0000        3452.         3.003
    .0000     -.0100        .0000        3040.         2.645
    .0000     -.0300        .0000        2107.         1.833
    .0000     -.0500        .0000        1636.         1.423
*  PPM CONCENTRATIONS CORRECT FOR CARBON MONOXIDE ONLY.
```

APPENDIX B. FORTRAN SOURCE PROGRAM LISTING FOR BATCH VERSION OF HIWAY

```
C        HIWAY - NEW VERSION - JUNE 1974
C        THIS PROGRAM CALCULATES THE CONCENTRATION FROM A LINE SOURCE
      COMMON /SOL/ QLN(25),HLN(25), RAQ(25),SAQ(25),RBQ(25),SBQ(25),
     *SYON,SZON,CON(50)
      COMMON /REC/ RR(51),SR(51),ZR(51)
      COMMON /WEA/ THETA,U,KST,HL
      COMMON /PUT/ XXRR(51),XXSR(51),QLS(25),HEAD(20),IWRI
      DIMENSION Z(51)
      IVERS=74250
      IRD=5
      IWRI = 6
C        READ HEADER CARD
10    READ(IRD,500,END=190)HEAD
500   FORMAT(20A4)
      WRITE(IWRI,510)HEAD
510   FORMAT('0',/,20A4,/)
      WRITE(IWRI,520)IVERS
520   FORMAT('0  HIWAY VERSION:',I6)
      READ(IRD,540,END=190) REP1,SEP1,REP2,SEP2,H,WIDTH,CNTR,XNL
540   FORMAT(8F10.0)
C        REP1,SEP1 ARE THE COORDINATES OF AN END POINT OF THE LINE
C          SOURCE IN SOURCE COORDINATES.
C        REP2,SEP2 ARE THE COORDINATES OF THE OTHER END POINT OF THE
C          LINE SOURCE IN SOURCE COORDINATES.
C        H IS THE EFFECTIVE EMISSION HEIGHT OF THE SOURCE IN METERS.
C        WIDTH IS THE HIGHWAY WIDTH (M) FOR AT GRADE
C        CNTR IS THE WIDTH OF THE CENTER STRIP (M)
C        XNL IS THE NUMBER OF LANES FOR THE AT-GRADE HIGHWAY.
      WRITE(IWRI,550)REP1,SEP1,REP2,SEP2
550   FORMAT(' ENDPOINTS OF THE LINE SOURCE',/,
     *F9.3,',',F9.3,' AND',F9.3,',',F9.3)
      NL=XNL
      WRITE(IWRI,560)H
560   FORMAT (' EMISSION HEIGHT IS',F8.3,' METERS')
      WRITE(IWRI,570)NL
570   FORMAT(' EMISSION RATE (GRAMS/SECOND*METER) OF',I4,' LANE(S)')
      READ(IRD,540)(QLS(I),I=1,NL)
```

```
C        QLS IS THE LINE SURCE STRENGTH (GRAMS/SECOND*METER)                   HIWAY
      WRITE(IWRI,580)(QLS(I),I=1,NL)                                        25 HIWAY
  580 FORMAT(8E12.3)                                                        26 HIWAY
      READ(IRD,540)CUT,WIDTC                                                27 HIWAY
C          CUT SECTION.                                                        HIWAY
C          WIDTC IS THE WIDTH OF THE TOP OF THE CUT SECTION (M)                HIWAY
      IF(CUT.EQ.0.)GOTO40                                                   28 HIWAY
C        DQLS IS THE CUT SECTION SOURCE STRENGTH                               HIWAY
      DQLS=0.                                                               29 HIWAY
      DO 20 I=1,NL                                                          30 HIWAY
   20 DQLS=DQLS+QLS(I)                                                      31 HIWAY
      XNDL=10.                                                              32 HIWAY
      NL=XNDL                                                               33 HIWAY
      DQLS=DQLS/XNDL                                                        34 HIWAY
      WRITE(IWRI,590)WIDTC                                                  35 HIWAY
  590 FORMAT(' WIDTH OF TOP OF CUT SECTION IS',F10.3,' M')                  36 HIWAY
      DO 30 I=1,NL                                                          37 HIWAY
   30 QLS(I)=DQLS                                                           38 HIWAY
      WIDTH=WIDTC                                                           39 HIWAY
      XNL=XNDL                                                              40 HIWAY
      CNTR=0.                                                               41 HIWAY
      GO TO 50                                                              42 HIWAY
   40 WRITE(IWRI,600)WIDTH,CNTR                                             43 HIWAY
  600 FORMAT(' WIDTH OF AT-GRADE HIGHWAY IS',F10.1,' M',/,                  44 HIWAY
     *' WIDTH OF CENTER STRIP IS',F10.1,' M')                                  HIWAY
   50 READ(IRD,540) THETA,U,HL,XKST                                         45 HIWAY
      KST=XKST                                                              46 HIWAY
C        THETA IS THE WIND DIRECTION IN DEGREES.                               HIWAY
C        U IS THE WIND SPEED IN METERS PER SECOND.                             HIWAY
C        KST IS THE STABILITY CLASS                                            HIWAY
C        HL IS THE HEIGHT OF THE LIMITING LID                                  HIWAY
   60 WRITE (IWRI,610) THETA,U,KST,HL                                       47 HIWAY
  610 FORMAT (' WIND DIRECTION IS',F7.0,'  DEGREES',/,' WIND SPEED IS',     48 HIWAY
     *F7.1,' METERS/SEC'/' STABILITY CLASS IS',I5,/,' HEIGHT OF LIMITING       HIWAY
     * LID IS',F8.1,' METERS')                                                 HIWAY
      READ(IRD,540)GS                                                       49 HIWAY
C        GS IS THE MEASURE BETWEEN COORDINATES (KM).                           HIWAY
```

```
      WRITE(IWRI,620)GS                                                          HIWAY 75
620   FORMAT(' THE SCALE OF THE COORDINATE AXES IS ',F10.4,' USER UNITS/         HIWAY 76
     *KM.' //)                                                                   HIWAY 77
      WRITE(IWRI,630)                                                            HIWAY 78
630   FORMAT(1H0,'   RECEPTOR LOCATION       HEIGHT      CONCENTRATION',/,       HIWAY 79
     *'         X',10X,'Y            Z(M)     UGM/METER**3      PPM  ')           HIWAY 80
      RA=REP1*GS                                                                 HIWAY 81
      RB=REP2*GS                                                                 HIWAY 82
      SA=SEP1*GS                                                                 HIWAY 83
      SB=SEP2*GS                                                                 HIWAY 84
      WL= (WIDTH-CNTR)/XNL                                                       HIWAY 85
      IF (CUT.GT.0.) GO TO 80                                                    HIWAY 86
70    SYON=3.                                                                    HIWAY 87
      SZON=1.5                                                                   HIWAY 88
      GO TO 100                                                                  HIWAY 89
80    IF (U.GT.3.) GO TO 70                                                      HIWAY 90
      IF (U.LT.1.) GO TO 90                                                      HIWAY 91
      DUM= (U-1.)/2.                                                             HIWAY 92
      SYON=10.-7.*DUM                                                            HIWAY 93
      SZON=5.-3.5*DUM                                                            HIWAY 94
      GO TO 100                                                                  HIWAY 95
90    SYON=10.                                                                   HIWAY 96
      SZON=5.                                                                    HIWAY 97
100   CONTINUE                                                                   HIWAY 98
      DELR=RB-RA                                                                 HIWAY 99
      DELS=SB-SA                                                                 HIWAY100
      DIST=SQRT(DELS*DELS+DELR*DELR)                                             HIWAY101
      NLIM=NL/2                                                                  HIWAY102
      ALIM=NLIM                                                                  HIWAY103
      DO 110 ID=1,NLIM                                                           HIWAY104
      A=ID                                                                       HIWAY105
      DL=(-0.5)*CNTR+((-1)*ALIM-0.5+A)*WL                                        HIWAY106
      DUM= DL*0.001/DIST                                                         HIWAY107
      RAQ(ID)=RA+DELS*DUM                                                        HIWAY108
      RBQ(ID)=RB+DELS*DUM                                                        HIWAY109
      SAQ(ID)=SA-DELR*DUM                                                        HIWAY110
      SBQ(ID)=SB-DELR*DUM                                                        HIWAY111
      QLN(ID)=QLS(ID)                                                   85 HIWAY1
      HLN(ID)=H                                                         86 HIWAY1
  110 CONTINUE                                                          87 HIWAY1
      NS=NLIM+1                                                         88 HIWAY1
      AS=NS                                                             89 HIWAY1
      DO 120 ID=NS,NL                                                   90 HIWAY1
      A=ID                                                              91 HIWAY1
      DL=0.5*CNTR+(0.5+A-AS)*WL                                         92 HIWAY1
      DUM=DL*0.001/DIST                                                 93 HIWAY1
      RAQ(ID)=RA+DELS*DUM                                               94 HIWAY1
      RBQ(ID)=RB+DELS*DUM                                               95 HIWAY1
      SAQ(ID)=SA-DELR*DUM                                               96 HIWAY1
      SBQ(ID)=SB-DELR*DUM                                               97 HIWAY1
      QLN(ID)=QLS(ID)                                                   98 HIWAY1
      HLN(ID)=H                                                         99 HIWAY1
  120 CONTINUE                                                         100 HIWAY1
      K=NL                                                             101 HIWAY1
      ICHK=1                                                           102 HIWAY1
      N=1                                                              103 HIWAY1
  130 READ(IRD,540,END=150)XXRR(N),XXSR(N),Z(N)                        104 HIWAY1
      IF(XXRR(N).GE.9999.)GO TO 170                                    105 HIWAY1
      IF(N-51)160,140,140                                              106 HIWAY1
  140 WRITE(IWRI,640)                                                  107 HIWAY1
  640 FORMAT(1H0,'THE NUMBER OF RECEPTORS IS LIMITED TO 50. YOU HAVE AT 108 HIWAY1
     *TEMPTED TO READ THE 51ST. COMPUTATIONS WILL BE MADE FOR 50.')        HIWAY1
  150 ICHK=2                                                           109 HIWAY1
      GO TO 170                                                        110 HIWAY1
  160 RR(N)=XXRR(N)*GS                                                 111 HIWAY1
      SR(N)=XXSR(N)*GS                                                 112 HIWAY1
      ZR(N)=Z(N)                                                       113 HIWAY1
      N=N+1                                                            114 HIWAY1
      GO TO 130                                                        115 HIWAY1
  170 N=N-1                                                            116 HIWAY1
      DO 180 IDUM=1,N                                                  117 HIWAY1
  180 CON(IDUM)=0.                                                     118 HIWAY1
C     K IS NUMBER OF LINE SOURCES                                          HIWAY1
C     N IS NUMBER OF RECEPTORS                                             HIWAY1
```

```
      CALL DBTLNE(K,N)
      WRITE(IWRI,650)                                                   119 HIWAY149
650   FORMAT(1H0,". PPM CONCENTRATIONS CORRECT FOR CARBON MONOXIDE ONLY 120 HIWAY150
     *.")                                                               121 HIWAY151
      GO TO (10,190),ICHK                                                   HIWAY152
190   CALL EXIT                                                         122 HIWAY153
      END                                                               123 HIWAY154
                                                                        124 HIWAY155

 22  COMMENT CARDS           9  CONTINUATION CARDS          34 NUMBERED STATEMENTS
```

```
      SUBROUTINE DBTLNE(NQ,NR)                                           HIWAY15
      COMMON /SOL/ GLN(25),HLN(25),RAQ(25),SAQ(25),RBQ(25),SBQ(25),      HIWAY15
     *SYON,SZON,CON(50)                                                  HIWAY15
      COMMON /REC/ RR(51),SR(51),ZR(51)                                  HIWAY15
      COMMON /WEA/ THETA,U,KST,HL                                        HIWAY16
      COMMON /PUT/ XXRR(51),XXSR(51),QLS(25),HEAD(20),IWRI               HIWAY16
      DIMENSION XST(11),YST(11)                                          HIWAY16
      X(R,S) = (R-RREC)*SINT + (S-SREC)*COST                             HIWAY16
C        X IS UPWIND DISTANCE OF R,S FROM RREC,SREC                      HIWAY16
      Y(R,S) = (S-SREC)*SINT - (R-RREC)*COST                             HIWAY16
C        Y IS CROSSWIND DISTANCE OF R,S FROM RREC,SREC                   HIWAY16
      TR = THETA/57.2958                                                 HIWAY16
      SINT = SIN(TR)                                                     HIWAY16
      COST = COS(TR)                                                     HIWAY16
      PIN=0.02                                                           HIWAY17
      UZ=U                                                               HIWAY17
      XVYL=XVY(SYON,KST)                                                 HIWAY17
      XVZL=XVZ(SZON,KST)                                                 HIWAY17
      DO 465 NC=1,NR                                                     HIWAY17
      RREC=RR(NC)                                                        HIWAY17
      SREC=SR(NC)                                                        HIWAY17
      Z=ZR(NC)                                                           HIWAY17
      DO 470 NS=1,NQ                                                     HIWAY17
      R1 = RAQ(NS)                                                       HIWAY17
      S1 = SAQ(NS)                                                       HIWAY18
      R2 = RBQ(NS)                                                       HIWAY18
      S2 = SBQ(NS)                                                       HIWAY18
      QL = QLN(NS)                                                       HIWAY18
      H = HLN(NS)                                                        HIWAY18
      X1 = X(R1,S1)                                                      HIWAY18
      X2 = X(R2,S2)                                                      HIWAY18
      IF (X1) 35,45,45                                                   HIWAY18
35    IF (X2) 40,45,45                                                   HIWAY18
40    RC = 0.                                                            HIWAY18
      GO TO 470                                                          HIWAY19
   45 IF (X1-100.)46,46,47                                               HIWAY19
   46 IF (X2-100.)49,49,47                                               HIWAY19
   47 WRITE(IWRI,48)
   48 FORMAT(1H0,'THIS RECEPTOR IS 100KM OR MORE FROM SOURCE')            35 HIWAY193
      GO TO 465                                                           36 HIWAY194
   49 DELR =R2-R1                                                         37 HIWAY195
      DELS = S2 - S1                                                      38 HIWAY196
      Y1 = Y(R1,S1)                                                       39 HIWAY197
      Y2 = Y(R2,S2)                                                       40 HIWAY198
      IF(Y1-Y2) 100,255,100                                               41 HIWAY199
C        IF Y1 = Y2, LINE SOURCE IS PARALLEL TO UPWIND AZIMUTH FROM RECE  42 HIWAY200
                                                                             HIWAY201
  100 IF(COST + 0.0001)135,105,165                                        43 HIWAY202
  105 IF(COST - 0.0001)110,110,135                                        44 HIWAY203
  110 IF(DELR + 0.0001)125,115,115                                        45 HIWAY204
  115 IF(DELR - 0.0001) 120,120,125                                       46 HIWAY205
  120 SLOC = SREC                                                         47 HIWAY206
      RLOC = R1                                                           48 HIWAY207
      GO TO 200                                                           49 HIWAY208
  125 SLP = DELS/DELR                                                     50 HIWAY209
      IF(SLP)130,255,130                                                  51 HIWAY210
  130 SLOC = SREC                                                         52 HIWAY211
      RLOC = (SLOC - S1)/SLP + R1                                         53 HIWAY212
      GO TO 200                                                           54 HIWAY213
  135 IF(SINT + 0.0001)160,140,140                                        55 HIWAY214
  140 IF(SINT - 0.0001)145,145,160                                        56 HIWAY215
  145 IF(DELR + 0.0001)155,150,150                                        57 HIWAY216
  150 IF(DELR - 0.0001)255,255,155                                        58 HIWAY217
  155 SLP = DELS/DELR                                                     59 HIWAY218
      RLOC = RREC                                                         60 HIWAY219
      SLOC = SLP * (RLOC - R1) + S1                                       61 HIWAY220
      GO TO 200                                                           62 HIWAY221
  160 IF(DELR + 0.0001)175,165,165                                        63 HIWAY222
  165 IF(DELR - 0.0001)170,170,175                                        64 HIWAY223
  170 RLOC = R1                                                           65 HIWAY224
      SLOC = (RLOC - RREC) * COST/SINT + SREC                             66 HIWAY225
      GO TO 200                                                           67 HIWAY226
  175 IF(DELS + 0.0001)190,180,180                                        68 HIWAY227
  180 IF(DELS - 0.0001)185,190,190                                        69 HIWAY228
  185 SLOC = S1                                                           70 HIWAY229
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      RLOC = (SLOC - SREC) * SINT/COST + RREC
      GO TO 200
190   TATH = SINT/COST
C        TATH IS TANGENT (THETA)
      SLP = DELS/DELR
C        SLP IS SLOPE OF LINE SOURCE.
      RLOC = (RREC/TATH + S1 - SLP*R1 - SREC)/ (1./TATH - SLP)
      SLOC = (RLOC - RREC)/TATH + SREC
C        RLOC, SLOC IS LOCUS OF UPWIND VECTOR FROM RECEPTOR AND LINEAR
C            EXTENSION OF LINE SOURCE.
200   XLOC = X(RLOC,SLOC)
      IF (XLOC)255,255,205
C        XLOC IS POSITIVE IF LOCUS IS UPWIND.
205   IF(S2-S1)210,210,215
210   SMAX = S1
      SMIN = S2
      GO TO 220
215   SMAX = S2
      SMIN = S1
220   IF(R2-R1)225,225,230
225   RMAX = R1
      RMIN = R2
      GO TO 235
230   RMAX = R2
      RMIN = R1
C        SEE IF UPWIND LOCUS IS ON LINE SOURCE.
235   IF(RLOC-RMIN)255,240,240
240   IF(RMAX-RLOC)255,245,245
245   IF(SLOC-SMIN)255,250,250
250   IF(SMAX-SLOC)255,260,260
255   INDIC = 1
C        INDIC =1 FOR NO LOCUS ON LINE SOURCE.
      XA = X1
      YA = Y1
      XB = X2
      YB = Y2
      GO TO 300
```

```
260   INDIC = 2                                                    101 HIWAY267
C        INDIC =2 FOR LOCUS ON LINE SOURCE.                            HIWAY268
      XA = X1                                                      102 HIWAY269
      YA = Y1                                                      103 HIWAY270
      XB = XLOC                                                    104 HIWAY271
      YB = 0.                                                      105 HIWAY272
300   DISX = XB - XA                                               106 HIWAY273
      DISY = YB - YA                                               107 HIWAY274
      DISI = SQRT (DISX*DISX + DISY*DISY)                          108 HIWAY275
C        DISI IS LENGTH(KM) OF LINE CONSIDERED.                        HIWAY276
      IF (DISI) 310,305,310                                        109 HIWAY277
305   CURR = 0.                                                    110 HIWAY278
      GO TO 435                                                    111 HIWAY279
310   DDI = DISI*1000./20.                                         112 HIWAY280
C        ONE-HALF IS INCLUDED IN THE 20.                               HIWAY281
C        DDI IS ONE-HALF TIMES 1/10 OF DISI (M).                       HIWAY282
      DX = DISX/10.                                                113 HIWAY283
      DY = DISY/10.                                                114 HIWAY284
      PREV =0.                                                     115 HIWAY285
      KNTRL = 1                                                    116 HIWAY286
      XI = XA                                                      117 HIWAY287
      YI = YA                                                      118 HIWAY288
      KNT = 0                                                      119 HIWAY289
      DO 355 I = 1,11                                              120 HIWAY290
C        STORE EACH XI,YI.                                             HIWAY291
      XST(I) = XI                                                  121 HIWAY292
      YST(I) = YI                                                  122 HIWAY293
      XZ = XI + XVZL                                               123 HIWAY294
      XY = XI + XVYL                                               124 HIWAY295
      CALL DBTRCX(UZ,Z,H,HL,XZ,XY,YI,KST,AN,M,SY,SZ,RC)            125 HIWAY296
      GO TO(315,335),KNTRL                                         126 HIWAY297
C        IF RC IS ZERO, CONTINUE UNTIL RC IS POSITIVE.                 HIWAY298
315   IF (RC) 350,350,320                                          127 HIWAY299
320   IF (I-1)325,325,330                                          128 HIWAY300
325   KNTRL = 2                                                    129 HIWAY301
      GO TO 345                                                    130 HIWAY302
C        RESET POINT A TO LAST ONE PREVIOUS.                           HIWAY303
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```
330   XA = XST(I-1)
      YA = YST(I-1)
      KNTRL = 2
      GO TO 345
335   IF(RC)340,340,345
C        RESET POINT B IF REACH ZERO CONCENTRATION.
340   XB = XI
      YB = YI
      GO TO 360
345   KNT = KNT + 1
350   XI = XI + DX
      YI = YI + DY
355   CONTINUE
360   IF(KNT)370,370,365
365   IF(KNT-6)300,300,390
C        IF GET TO 370, CONC. FROM THIS SEGMENT IS 0.
370   GO TO (375,380,385),INDIC
375   RC = 0.
      GO TO 465
380   FIRST = 0.
      GO TO 450
385   RC = FIRST
      GO TO 460
390   CONTINUE
C        DO  A TRAPEZOIDAL INTEGRATION FROM A TO B IN TEN STEPS.
C        IT IS LIKELY THAT A OR B HAVE BEEN REDEFINED.
400   DISX = XB-XA
      DISY = YB-YA
      DISI = SQRT(DISX*DISX + DISY*DISY)
C        DISI IS DISTANCE(KM) FROM A TO B
      DELD = DISI*100.
C        DELD IS 1/10 DISI IN METERS.
      DX = DISX/10.
      DY = DISY/10.
      SUM = 0.
      XDUM = XA
      YDUM = YA
      XZ = XDUM + XVZL                                                  HIWAY341
      XY = XDUM + XVYL                                                  HIWAY342
      CALL DBTRCX(UZ,Z,H,HL,XZ,XY,YDUM,KST,AN,M,SY,SZ,RC)               HIWAY343
      SUM = SUM + RC/2.                                                 HIWAY344
      DO 405 I = 1,9                                                    HIWAY345
      XDUM = XDUM + DX                                                  HIWAY346
      YDUM = YDUM + DY                                                  HIWAY347
      XZ = XDUM + XVZL                                                  HIWAY348
      XY = XDUM + XVYL                                                  HIWAY349
      CALL DBTRCX(UZ,Z,H,HL,XZ,XY,YDUM,KST,AN,M,SY,SZ,RC)               HIWAY350
  405 SUM = SUM + RC                                                    HIWAY351
      XDUM = XDUM + DX                                                  HIWAY352
      YDUM = YDUM + DY                                                  HIWAY353
      XZ = XDUM + XVZL                                                  HIWAY354
      XY = XDUM + XVYL                                                  HIWAY355
      CALL DBTRCX(UZ,Z,H,HL,XZ,XY,YDUM,KST,AN,M,SY,SZ,RC)               HIWAY356
      SUM = SUM + RC/2.                                                 HIWAY357
C        INTEGRATED VALUE IS CURR.                                      HIWAY358
      CURR = SUM * DELD                                                 HIWAY359
      ILIM = 10                                                         HIWAY360
C     FIRST ESTIMATE COMPLETED HERE.                                    HIWAY361
  410 PREV = CURR                                                       HIWAY362
C        EVALUATE FOR POINTS IN BETWEEN THOSE ALREADY EVALUATED.        HIWAY363
      DELD = DELD/2.                                                    HIWAY364
      XDUM = XA + DX/2.                                                 HIWAY365
      YDUM = YA + DY/2.                                                 HIWAY366
      DO 415 I = 1,ILIM                                                 HIWAY367
      XZ = XDUM + XVZL                                                  HIWAY368
      XY = XDUM + XVYL                                                  HIWAY369
      CALL DBTRCX(UZ,Z,H,HL,XZ,XY,YDUM,KST,AN,M,SY,SZ,RC)               HIWAY370
C        NOTE ADD THESE TO RC'S FOUND ABOVE.                            HIWAY371
      SUM = SUM + RC                                                    HIWAY372
      XDUM = XDUM + DX                                                  HIWAY373
  415 YDUM = YDUM + DY                                                  HIWAY374
      CURR = SUM * DELD                                                 HIWAY375
C     SECOND ESTIMATE COMPLETED HERE. ALSO FOURTH,SIXTH,ETC.            HIWAY376
      TEST = ABS((CURR-PREV)/CURR)                                      HIWAY377
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```
C        IF WITHIN PIN OF LAST VALUE (PREV), CONSIDER THIS AS FINAL VALU
      IF(TEST-PIN)435,420,420
420   ILIM = ILIM * 2
      PREV = CURR
C        EVALUATE POINTS IN BETWEEN.
      DELD = DELD/2.
      DX = DX/2.
      DY = DY/2.
      XDUM = XA + DX/2.
      YDUM = YA + DY/2.
      DO 425 I = 1,ILIM
      XZ = XDUM + XVZL
      XY = XDUM + XVYL
      CALL DBTRCX(UZ,Z,H,HL,XZ,XY,YDUM,KST,AN,M,SY,SZ,RC)
      SUM = SUM + RC
      XDUM = XDUM +DX
425   YDUM = YDUM +DY
      CURR = SUM * DELD
C        THIRD ESTIMATE COMPLETED HERE. ALSO FIFTH,SEVENTH, ETC.
      TEST = ABS((CURR-PREV)/CURR)
      IF (TEST-PIN)435,430,430
430   ILIM = ILIM * 2
      DX = DX/2.
      DY = DY/2.
      GO TO 410
C        AT 435 HAVE FINAL VALUE OF INTEGRATION IN CURR.
435   GO TO (440,445,455),INDIC
440   RC = CURR
      GO TO 460
445   FIRST = CURR
450   INDIC = 3
      XA = XLOC
      YA = 0.
      XB = X2
      YB = Y2
      GO TO 300
455   RC = FIRST + CURR
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460    CON(NC)=CON(NC)+RC*QL
470    CONTINUE                                                        227 HIWAY415
       CON(NC)=1.0E+6*CON(NC)                                          228 HIWAY416
       CLSS=0.0087*CON(NC)                                             229 HIWAY417
       WRITE(IWRI,660)XXRR(NC),XXSR(NC),ZR(NC),CON(NC),CLSS            230 HIWAY418
660    FORMAT(1H ,3(F10.4,2X),F10.0,F10.3)                             231 HIWAY419
465    CONTINUE                                                        232 HIWAY420
       RETURN                                                          233 HIWAY421
       END                                                             234 HIWAY422
                                                                       235 HIWAY423
 32  COMMENT CARDS          1  CONTINUATION CARDS        74 NUMBERED STATLMENTS
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      SUBROUTINE DBTRCX (U,Z,H,HL,X,XY,Y,KST,AN,M,SY,SZ,RC)             1 HIWAY424
C       THIS IS THE 1972 VERSION OF DBTRCX.                                HIWAY425
C       SUBROUTINE DBTRCX CALCULATES CHI/Q CONCENTRATION VALUES, DBTRCX    HIWAY426
C         CALLS UPON SUBROUTINE DBTSIG TO OBTAIN STANDARD DEVIATIONS.      HIWAY427
C       THE INPUT VARIABLES ARE....                                        HIWAY428
C         U     WIND SPEED (M/SEC)                                         HIWAY429
C         Z     RECEPTOR HEIGHT (M)                                        HIWAY430
C         H     EFFECTIVE STACK HEIGHT (M)                                 HIWAY431
C         HL=L  HEIGHT OF LIMITING LID (M)                                 HIWAY432
C         X     DISTANCE RECEPTOR IS DOWNWIND OF SOURCE (KM)               HIWAY433
C         XY    X+VIRTUAL DISTANCE USED FOR AREA SOURCE APPROX. (KM)       HIWAY434
C         Y     DISTANCE RECEPTOR IS CROSSWIND FROM SOURCE (KM)            HIWAY435
C         KST   STABILITY CLASS                                            HIWAY436
C       THE OUTPUT VARIABLES ARE....                                       HIWAY437
C         AN    THE NUMBER OF TIMES THE SUMMATION TERM IS EVALUATED        HIWAY438
C                 AND ADDED IN.                                            HIWAY439
C         RC    RELATIVE CONCENTRATION (SEC/M**3)                          HIWAY440
C       IWRI IS CONTROL CODE FOR OUTPUT                                    HIWAY441
      IWRI = 6                                                          2 HIWAY442
C       THE FOLLOWING EQUATION IS SOLVED --                                HIWAY443
C         RC = (1/(2*PI*U*SIGMA Y*SIGMA Z))* (EXP(-0.5*(Y/SIGMA Y)**2))    HIWAY444
C           (EXP(-0.5*((Z-H)/SIGMA Z)**2) + EXP(-0.5*((Z+H)/SIGMA Z)**2)   HIWAY445
C             PLUS THE SUM OF THE FOLLOWING 4 TERMS K TIMES (N=1,K) --     HIWAY446
C               TERM 1- EXP(-0.5*((Z-H-2NL)/SIGMA Z)**2)                   HIWAY447
C               TERM 2- EXP(-0.5*((Z+H-2NL)/SIGMA Z)**2)                   HIWAY448
C               TERM 3- EXP(-0.5*((Z-H+2NL)/SIGMA Z)**2)                   HIWAY449
C               TERM 4- EXP(-0.5*((Z+H+2NL)/SIGMA Z)**2)                   HIWAY450
C       THE ABOVE EQUATION IS SIMILAR TO EQUATION (5.8) P 36 IN            HIWAY451
C         WORKBOOK OF ATMOSPHERIC DISPERSION ESTIMATES WITH THE ADDITION   HIWAY452
C         OF THE EXPONENTIAL INVOLVING Y.                                  HIWAY453
C       IF THE SOURCE IS ABOVE THE LID, SET RC = 0., AND RETURN.           HIWAY454
      IF (H-HL)302,302,304                                              3 HIWAY455
302   IF (Z-HL)300,300,30                                               4 HIWAY456
304   IF (Z-HL)30,306,306                                               5 HIWAY457
306   WRITE(IWRI, 307)                                                  6 HIWAY458
307   FORMAT (1H0,'BOTH H AND Z ARE ABOVE THE MIXING HEIGHT SO A RELIABL 7 HIWAY459
     *E COMPUTATION CAN NOT BE MADE.')                                    HIWAY460
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30     RC =0.
       RETURN                                                          8 HIWAY461
C         IF X IS LESS THAN 1 METER, SET RC=0. AND RETURN.  THIS AVOIDS  9 HIWAY462
C           PROBLEMS OF INCORRECT VALUES NEAR THE SOURCE.                 HIWAY463
300    IF (X-0.001)30,310,310                                            HIWAY464
C         CALL DBTSIG TO OBTAIN VALUES FOR SY AND SZ                   10 HIWAY465
310    CALL DBTSIG (X,XY,KST,SY,SZ)                                      HIWAY466
C         SY = SIGMA Y, THE STANDARD DEVIATION OF CONCENTRATION IN THE  11 HIWAY467
C         Y-DIRECTION (M)                                                HIWAY468
C         SZ = SIGMA Z, THE STANDARD DEVIATION OF CONCENTRATION IN THE     HIWAY469
C         Z-DIRECTION (M)                                                HIWAY470
       C1 = 1.                                                           HIWAY471
       IF ( Y)5,400,5                                                 12 HIWAY472
5      YD = 1000. * Y                                                 13 HIWAY473
C         YD IS CROSSWIND DISTANCE IN METERS.                         14 HIWAY474
C                                                                        HIWAY475
       DUM = YD/SY                                                       HIWAY476
       TEMP = 0.5*DUM*DUM                                             15 HIWAY477
       IF ( TEMP-50.)6,30,30                                          16 HIWAY478
6      C1 = EXP(TEMP)                                                 17 HIWAY479
400    IF (KST-4)401,401,403                                          18 HIWAY480
401    IF (HL-5000.)7,403,403                                         19 HIWAY481
C         IF STABLE CONDITION OR UNLIMITED MIXING HEIGHT,             20 HIWAY482
C         USE EGUATION 3.2 IF Z = 0, OR EQ 3.1 FOR NON-ZERO Z.           HIWAY483
403    C2 = 2.*SZ*SZ                                                     HIWAY484
       IF (Z)30,404,406                                               21 HIWAY485
404    C3 = H*H/C2                                                    22 HIWAY486
       IF (C3-50.)405,30,30                                           23 HIWAY487
405    A2= 1./EXP(C3)                                                 24 HIWAY488
C         WADE EQUATION 3.2.                                          25 HIWAY489
       RC = A2/(3.14159*U*SY*SZ*C1)                                      HIWAY490
       M = 1                                                          26 HIWAY491
       RETURN                                                         27 HIWAY492
406    A2 = 0.                                                        28 HIWAY493
       A3 = 0.                                                        29 HIWAY494
       CA = Z-H                                                       30 HIWAY495
       CB = Z+H                                                       31 HIWAY496
                                                                      32 HIWAY497
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      C3 = CA*CA/C2                                                     33 HIWAY498
      C4 = CB*CB/C2                                                     34 HIWAY499
      IF (C3-50.) 407,408,408                                           35 HIWAY500
407   A2 = 1./EXP(C3)                                                   36 HIWAY501
408   IF (C4-50.) 409,411,411                                           37 HIWAY502
409   A3 = 1./EXP(C4)                                                   38 HIWAY503
C        WADE EQUATION 3.1.                                                HIWAY504
411   RC = (A2 + A3)/(6.28318*U*SY*SZ*C1)                               39 HIWAY505
      M = 2                                                             40 HIWAY506
      RETURN                                                            41 HIWAY507
C        IF SIGMA-Z IS GREATER THAN 1.6 TIMES THE MIXING HEIGHT,           HIWAY508
C          THE DISTRIBUTION BELOW THE MIXING HEIGHT IS UNIFORM WITH        HIWAY509
C          HEIGHT REGARDLESS OF SOURCE HEIGHT.                             HIWAY510
7     IF (SZ/HL - 1.6) 9,9,8                                            42 HIWAY511
C        WADE EQUATION 3.5.                                                HIWAY512
8     RC = 1./(2.5066*U*SY*HL*C1)                                       43 HIWAY513
      M = 3                                                             44 HIWAY514
      RETURN                                                            45 HIWAY515
C        INITIAL VALUE OF AN SET = 0.                                      HIWAY516
9     AN = 0.                                                           46 HIWAY517
      IF (Z) 30,340,40                                                  47 HIWAY518
C        STATEMENTS 40 TO 250 CALCULATE RC, THE RELATIVE CONCENTRATION,    HIWAY519
C          USING THE EQUATION DISCUSSED ABOVE.  SEVERAL INTERMEDIATE       HIWAY520
C          VARIABLES ARE USED TO AVOID REPEATING CALCULATIONS.             HIWAY521
C          CHECKS ARE MADE TO BE SURE THAT THE ARGUMENT OF THE             HIWAY522
C          EXPONENTIAL FUNCTION IS NEVER GREATER THAN 50 (OR LESS THAN     HIWAY523
C          -50).  IF 'AN' BECOMES GREATER THAN 45, A LINE OF OUTPUT IS     HIWAY524
C          PRINTED INFORMING OF THIS.                                      HIWAY525
C        CALCULATE MULTIPLE EDDY REFLECTIONS FOR RECEPTOR HEIGHT Z.        HIWAY526
40    A1 = 1./(6.28318*U*SY*SZ*C1)                                      48 HIWAY527
      C2=2.*SZ*SZ                                                       49 HIWAY528
      A2 = 0.                                                           50 HIWAY529
      A3 = 0.                                                           51 HIWAY530
      CA = Z-H                                                          52 HIWAY531
      CB = Z+H                                                          53 HIWAY532
      C3 = CA*CA/C2                                                     54 HIWAY533
      C4 = CB*CB/C2                                                     55 HIWAY534
      IF ( C3 -50.)60,80,80                                          HIWAY535
 60   A2 =1./EXP(C3)                                                 HIWAY536
 80   IF (C4-50.) 90,110,110                                         HIWAY537
 90   A3 =1./EXP(C4)                                                 HIWAY538
 110  SUM= 0.                                                        HIWAY539
      THL = 2. * HL                                                  HIWAY540
 120  AN =AN+ 1.                                                     HIWAY541
      A4 = 0.                                                        HIWAY542
      A5 = 0.                                                        HIWAY543
      A6 = 0.                                                        HIWAY544
      A7 = 0.                                                        HIWAY545
      C5 = AN* THL                                                   HIWAY546
      CC = CA-C5                                                     HIWAY547
      CD = CB-C5                                                     HIWAY548
      CE = CA+ C5                                                    HIWAY549
      CF = CB+ C5                                                    HIWAY550
      C6 = CC* CC /C2                                                HIWAY551
      C7 = CD* CD /C2                                                HIWAY552
      C8 = CE* CE /C2                                                HIWAY553
      C9 = CF* CF /C2                                                HIWAY554
      IF (C6- 50.) 130,150,150                                       HIWAY555
 130  A4 =1./EXP(C6)                                                 HIWAY556
 150  IF (C7- 50.) 160,180,180                                       HIWAY557
 160  A5 =1./EXP(C7)                                                 HIWAY558
 180  IF (C8- 50.) 190,210,210                                       HIWAY559
 190  A6 =1./EXP(C8)                                                 HIWAY560
 210  IF (C9- 50.) 220,240,240                                       HIWAY561
 220  A7 =1./EXP(C9)                                                 HIWAY562
 240  T= A4 +A5+ A6 +A7                                              HIWAY563
      SUM= SUM+ T                                                    HIWAY564
      IF ( T- 0.01 )250,120,120                                      HIWAY565
 250  RC =A1* (A2+ A3+SUM)                                           HIWAY566
      M = 5                                                          HIWAY567
      RETURN                                                         HIWAY568
C       CALCULATE MULTIPLE EDDY REFLECTIONS FOR GROUND LEVEL RECEPTOR H HIWAY569
 340  A1 = 1./(6.28318*U*SY*SZ*C1)                                   HIWAY570
      A2 = 0.                                                        HIWAY571
      C2 = 2.*SZ*SZ                                                 92 HIWAY572
      C3 = H*H/C2                                                   93 HIWAY573
      IF (C3-50.) 360,410,410                                       94 HIWAY574
360   A2 = 2./EXP(C3)                                               95 HIWAY575
410   SUM = 0.                                                      96 HIWAY576
      THL = 2. * HL                                                 97 HIWAY577
420   AN = AN + 1.                                                  98 HIWAY578
      A4 = 0.                                                       99 HIWAY579
      A6 = 0.                                                      100 HIWAY580
      C5 = AN*THL                                                  101 HIWAY581
      CC = H-C5                                                    102 HIWAY582
      CE = H + C5                                                  103 HIWAY583
      C6 = CC*CC/C2                                                104 HIWAY584
      C8 = CE*CE/C2                                                105 HIWAY585
      IF (C6-50.) 430,480,480                                      106 HIWAY586
430   A4 = 2./EXP(C6)                                              107 HIWAY587
480   IF (C8-50.) 490,540,540                                      108 HIWAY588
490   A6 = 2./EXP(C8)                                              109 HIWAY589
540   T = A4 + A6                                                  110 HIWAY590
      SUM = SUM + T                                                111 HIWAY591
      IF (T-0.01) 550,420,420                                      112 HIWAY592
550   RC = A1 * (A2 + SUM)                                         113 HIWAY593
      M = 4                                                        114 HIWAY594
      RETURN                                                       115 HIWAY595
      END                                                          116 HIWAY596

 56  COMMENT CARDS          1   CONTINUATION CARDS          41 NUMBERED STATEMENTS
```

```
      SUBROUTINE DBTSIG (X,XY,KST,SY,SZ)                                  HIWAY597
      DIMENSION XA(7),XB(2),XD(5),XE(8),XF(9),AA(8),BA(8),AB(3),BB(3),    HIWAY598
     * AD(6),BD(6),AE(9),BE(9),AF(10),BF(10)                              HIWAY599
      DATA XA/.5,.4,.3,.25,.2,.15,.1/                                     HIWAY600
      DATA XB/.4,.2/                                                      HIWAY601
      DATA XD /30.,10.,3.,1.,.3/                                          HIWAY602
      DATA XE /40.,20.,10.,4.,2.,1.,.3,.1/                                HIWAY603
      DATA XF /60.,30.,15.,7.,3.,2.,1.,.7,.2/                             HIWAY604
      DATA AA /453.85,346.75,258.89,217.41,179.52,170.22,158.08,122.8/    HIWAY605
      DATA BA /2.1166,1.7283,1.4094,1.2644,1.1262,1.0932,1.0542,.9447/    HIWAY606
      DATA AB /109.30,98.483,90.673/                                      HIWAY607
      DATA BB /1.0971,0.98332,0.93198/                                    HIWAY608
      DATA AD /44.053,36.650,33.504,32.093,32.093,34.459/                 HIWAY609
      DATA BD /0.51179,0.56589,0.60486,0.64403,0.81066,0.86974/           HIWAY610
      DATA AE /47.618,35.420,26.970,24.703,22.534,21.628,21.628,23.331,   HIWAY611
     * 24.26/                                                             HIWAY612
      DATA BE /0.29592,0.37615,0.46713,0.50527,0.57154,0.63077,0.75660,   HIWAY613
     * 0.81956,0.8366/                                                    HIWAY614
      DATA AF /34.219,27.074,22.651,17.836,16.187,14.823,13.353,13.953,   HIWAY615
     * 14.457,15.209/                                                     HIWAY616
      DATA BF /0.21716,0.27436,0.32681,0.41507,0.46490,0.54503,0.63227,   HIWAY617
     * 0.68465,0.78407,0.81558/                                           HIWAY618
      GO TO (10,20,30,40,50,60),KST                                       HIWAY619
C        STABILITY A (10)                                                 HIWAY620
10    TH = (24.167 - 2.5334*ALOG(XY))/57.2958                             HIWAY621
      IF (X.GT.3.11) GO TO 69                                             HIWAY622
      DO 11 ID = 1,7                                                      HIWAY623
      IF(X.GE.XA(ID)) GO TO 12                                            HIWAY624
11    CONTINUE                                                            HIWAY625
      ID = 8                                                              HIWAY626
12    SZ = AA(ID) * X ** BA(ID)                                           HIWAY627
      GO TO 71                                                            HIWAY628
C        STABILITY B (20)                                                 HIWAY629
20    TH = (18.333 - 1.8096*ALOG(XY))/57.2958                             HIWAY630
      IF(X.GT.35.) GO TO 69                                               HIWAY631
      DO 21 ID = 1,2                                                      HIWAY632
      IF (X.GE.XB(ID)) GO TO 22                                           HIWAY633
```

```
21    CONTINUE                                              HIWAY634
      ID = 3                                                HIWAY635
22    SZ = AB(ID) * X ** BB(ID)                             HIWAY636
      GO TO 70                                              HIWAY637
C         STABILITY C (30)                                  HIWAY638
30    TH = (12.5 - 1.0857*ALOG(XY))/57.2958                 HIWAY639
      SZ = 61.141 *X ** 0.91465                             HIWAY640
      GO TO 70                                              HIWAY641
C         STABILITY D (40)                                  HIWAY642
40    TH = (8.3333-0.72382*ALOG(XY))/57.2958                HIWAY643
      DO 41 ID = 1,5                                        HIWAY644
      IF (X.GE.XD(ID)) GO TO 42                             HIWAY645
41    CONTINUE                                              HIWAY646
      ID = 6                                                HIWAY647
42    SZ = AD(ID) * X ** BD(ID)                             HIWAY648
      GO TO 70                                              HIWAY649
C         STABILITY E (50)                                  HIWAY650
50    TH = (6.25 - 0.54287*ALOG(XY))/57.2958                HIWAY651
      DO 51 ID = 1,8                                        HIWAY652
      IF (X.GE.XE(ID)) GO TO 52                             HIWAY653
51    CONTINUE                                              HIWAY654
      ID = 9                                                HIWAY655
52    SZ = AE(ID) * X ** BE(ID)                             HIWAY656
      GO TO 70                                              HIWAY657
C         STABILITY F (60)                                  HIWAY658
60    TH = (4.1667 - 0.36191*ALOG(XY))/57.2958              HIWAY659
      DO 61 ID = 1,9                                        HIWAY660
      IF (X.GE.XF(ID)) GO TO 62                             HIWAY661
61    CONTINUE                                              HIWAY662
      ID = 10                                               HIWAY663
62    SZ = AF(ID) * X ** BF(ID)                             HIWAY664
      GO TO 70                                              HIWAY665
69    SZ = 5000.                                            HIWAY666
      GO TO 71                                              HIWAY667
70    IF (SZ.GT.5000.) SZ = 5000.                           HIWAY668
71    SY = 1000. * XY * SIN(TH)/(2.15 * COS(TH))            HIWAY669
      RETURN                                                HIWAY670
      END                                                              64 HIWAY671
    6  COMMENT CARDS          5  CONTINUATION CARDS          19 NUMBERED STATEMENTS



      FUNCTION XVY (SYO,KST)                                            1 HIWAY672
      GO TO (1,2,3,4,5,6),KST                                           2 HIWAY673
 1    XVY = (SYO/213.)**1.1148                                          3 HIWAY674
      RETURN                                                            4 HIWAY675
 2    XVY = (SYO/155.)**1.097                                           5 HIWAY676
      RETURN                                                            6 HIWAY677
 3    XVY = (SYO/103.)**1.092                                           7 HIWAY678
      RETURN                                                            8 HIWAY679
 4    XVY = (SYO/68.)**1.076                                            9 HIWAY680
      RETURN                                                           10 HIWAY681
 5    XVY = (SYO/50.)**1.086                                           11 HIWAY682
      RETURN                                                           12 HIWAY683
 6    XVY = (SYO/33.5)**1.083                                          13 HIWAY684
      RETURN                                                           14 HIWAY685
      END                                                              15 HIWAY686
    0  COMMENT CARDS          0  CONTINUATION CARDS          6 NUMBERED STATEMENTS
```

```
      FUNCTION XVZ (SZO,KST)                                            HIWAY687
      DIMENSION SA(7),SB(2),SD(5),SE(8),SF(9),AA(8),AB(3),AD(6),AE(9),  HIWAY688
     * AF(10),CA(8),CB(3),CD(6),CE(9),CF(10)                            HIWAY689
      DATA SA /13.95,21.40,29.3,37.67,47.44,71.16,104.65/               HIWAY690
      DATA SB /20.23,40./                                               HIWAY691
      DATA SD /12.09,32.09,65.12,134.9,251.2/                           HIWAY692
      DATA SE /3.534,8.698,21.628,33.489,49.767,79.07,109.3,141.86 /    HIWAY693
      DATA SF /4.093,10.93,13.953,21.627,26.976,40.,54.89,68.84,83.25/  HIWAY694
      DATA AA /122.8,158.08,170.22,179.52,217.41,258.89,346.75,453.85/  HIWAY695
      DATA AB /90.673,98.483,109.3/                                     HIWAY696
      DATA AD /34.459,32.093,32.093,33.504,36.650,44.053/               HIWAY697
      DATA AE /24.26,23.331,21.628,21.628,22.534,24.703,26.97,35.42,    HIWAY698
     * 47.618/                                                          HIWAY699
      DATA AF /15.209,14.457,13.953,13.953,14.823,16.187,17.836,22.651, HIWAY700
     * 27.074,34.219/                                                   HIWAY701
      DATA CA /1.0585,.3486,.9147,.8879,.7909,.7095,.5786,.4725/        HIWAY702
      DATA CB /1.073,1.017,.9115/                                       HIWAY703
      DATA CD /1.1498,1.2336,1.5527,1.6533,1.7671,1.9539/               HIWAY704
      DATA CE /1.1953,1.2202,1.3217,1.5854,1.7497,1.9791,2.1407,2.6585, HIWAY705
     * 3.3793/                                                          HIWAY706
      DATA CF /1.2261,1.2754,1.4606,1.5816,1.8348,2.151,2.4092,3.0599,  HIWAY707
     * 3.6448,4.6049/                                                   HIWAY708
      GO TO (10,20,30,40,50,60),KST                                     HIWAY709
C        STABILITY A(10)                                                HIWAY710
10    DO 11 ID = 1,7                                                    HIWAY711
      IF(SZO.LE.SA(ID)) GO TO 12                                        HIWAY712
11    CONTINUE                                                          HIWAY713
      ID = 8                                                            HIWAY714
12    XVZ =(SZO/AA(ID))**CA(ID)                                         HIWAY715
      RETURN                                                            HIWAY716
C        STABILITY B (20)                                               HIWAY717
20    DO 21 ID = 1,2                                                    HIWAY718
      IF (SZO.LE.SB(ID)) GO TO 22                                       HIWAY719
21    CONTINUE                                                          HIWAY720
      ID = 3                                                            HIWAY721
22    XVZ = (SZO/AB(ID))**CB(ID)                                        HIWAY722
      RETURN                                                            HIWAY723
```

```
C         STABILITY C (30)
30     XVZ = (SZO/61.141)**1.0933                                      HIWAY724
       RETURN                                                       31 HIWAY725
C         STABILITY D (40)                                          32 HIWAY726
40     DO 41 ID = 1,5                                                  HIWAY727
       IF(SZO.LE.SD(ID)) GO TO 42                                   33 HIWAY728
41     CONTINUE                                                     34 HIWAY729
       ID = 5                                                       35 HIWAY730
42     XVZ = (SZO/AD(ID))**CD(ID)                                   36 HIWAY731
       RETURN                                                       37 HIWAY732
C         STABILITY E (50)                                          38 HIWAY733
50     DO 51 ID = 1,8                                                  HIWAY734
       IF (SZO.LE.SE(ID)) GO TO 52                                  39 HIWAY735
51     CONTINUE                                                     40 HIWAY736
       ID = 9                                                       41 HIWAY737
52     XVZ = (SZO/AE(ID))**CE(ID)                                   42 HIWAY738
       RETURN                                                       43 HIWAY739
C         STABILITY F(60)                                           44 HIWAY740
60     DO 61 ID = 1,9                                                  HIWAY741
       IF(SZO.LE.SF(ID)) GO TO 62                                   45 HIWAY742
61     CONTINUE                                                     46 HIWAY743
       ID = 10                                                      47 HIWAY744
62     XVZ = (SZO/AF(ID))**CF(ID)                                   48 HIWAY745
       RETURN                                                       49 HIWAY746
       END                                                          50 HIWAY747
                                                                    51 HIWAY748

  6  COMMENT CARDS          5  CONTINUATION CARDS          16 NUMBERED STATEMENTS
```

APPENDIX B6.3

LINE SOURCE MODELING

by

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Meteorology Laboratory

To Be Presented by L. E. Niemeyer* at the
5th Meeting of the Panel on Modeling
of the NATO Committee on the
Challenges of Modern Society

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* On Assignment from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce

LINE SOURCE MODELING

ABSTRACT

This paper discusses estimation of air pollutant concentrations from line sources such as highways and airport runways. Emphasized is the Gaussian plume approach applicable when there is undisturbed horizontal flow from the source to the receptor. Results are given for an example of the estimation of particulate sulfate concentrations from motor vehicles. Sensitivity to atmospheric stability and to the angle between wind direction and source orientation is shown. Sufficient comparisons have been made with field measurements to give some degree of confidence in the use of this model.

INTRODUCTION

This paper discusses the estimation of air pollution concentrations that result from line source emissions. Highways and airport runways are examples of such line sources. To estimate concentrations from these line sources, several different approaches have been used. These include use of Gaussian models and of cell models. Inputs to the models require information concerning the source geometry and its emissions, the meteorological conditions, and also the location of the receptor points. One of the primary needs for a line source model is to estimate concentrations from linear highway segments. These estimates are used in preparing environmental impact statements. Of major interest for impact statements are the meteorological conditions and angle of the wind with the roadway that lead to the highest concentrations.

An additional use of line source models is to determine the environmental impact of aircraft emissions from runways and taxiways.

APPROACHES

There are several different approaches to simulating dispersion from line sources. The approach that will be emphasized here is the use of Gaussian dispersion models. The Gaussian models assume that the distributions of pollutants in the crosswind and vertical directions are Gaussian or bell-shaped distributions. The Gaussian approach is limited to situations where the wind flow is horizontal and parallel to the ground, and a single representative wind speed can be chosen.

Situations that have been considered using the Gaussian model are "at-grade level" roads and also roads in "cut-sections." In the case of the "cut-section" roadway, it is assumed that the flow above the cut is essentially horizontal and estimates are only made for receptor points outside the cut.

Depending upon the angle between the wind direction and the roadway, and also upon the length of the roadway, either simple formulae or numerical integration procedures are used to estimate the concentrations at receptors. These are discussed below.

In applying the Gaussian model to highway segments, a separate line source and emission rate are used for each lane of traffic. To account for the initial dispersion in the turbulent wake behind each vehicle, an initial distribution of pollution is also assumed.

Air quality estimates are needed for averaging times of 1 hour or longer because of the averaging times of the air quality standards. Therefore, emissions averaged over hourly time periods are used. The averaging is done by determining total vehicle flow for each hour and the appropriate emission factor to obtain the average emission over each one-hour time period. Different emission rates can be used for each lane of traffic based on the number of vehicles using that particular lane.

Other approaches, such as the grid approach, as used in the EXPLOR Model, (Sklarew, Fabrick, and Prager, 1972) have also been applied to line sources. Cell models, using diffusivities for the dispersion, can account for variations in flow and the increase of wind speed with height. However, these will not be discussed in this paper.

INPUTS TO THE MODEL

There are three important inputs to the line source model. First, the location of the source and the emission rates must be known. In the case of a highway segment the coordinates of the end points of the segment, the number of lanes, the total width of the highway, and the width of any median are required. Emissions for each lane separately are entered as grams per second per meter of length. This line source emission rate, q_ℓ, can be found if the emission factor EF (g veh^{-1} km^{-1}) and the traffic volume TV (veh hr^{-1}) are known. The following equation similar to that from Zimmerman and Thompson (1974) is used:

$$q_\ell \; (\mathrm{g\ sec^{-1} m^{-1}}) = \frac{\mathrm{EF}\ (\mathrm{g\ \ veh^{-1}\ km^{-1}})\ \mathrm{TV}\ (\mathrm{veh\ hr^{-1}})}{1000.(\mathrm{m\ km^{-1}})\ 3600\ (\mathrm{sec\ hr^{-1}})}$$

$$= 2.78\mathrm{x}10^{-7}\ (\mathrm{EF})\ (\mathrm{TV})$$

A value for the emission factor can be obtained from the Second Edition of Compilation of Air Pollutant Emission Factors (EPA, 1973). When vehicle speed is known and different from that used in the reference, a multiplier correction factor is used.

The second category of input is meteorological conditions. Wind direction, wind speed, stability class, and mixing height are required for each hour. Since mixing height is the top of the neutral or unstable layer, it is not a valid concept for situations where stable conditions exist in the layer of atmosphere near the ground. Therefore, a value for mixing height is not considered for stable conditions.

The third classification of input is the location of receptors. The East and North coordinates and the height above ground (usually zero) are needed.

Calculation of Concentrations

For the special situation of the wind direction perpendicular to the line source with the end points of the line at some distances from the location of interest, the Gaussian Model is a simple equation:

$$\chi = \sqrt{\frac{2}{\pi}} \frac{q_\ell}{u\,\sigma_z(x + a)} \qquad (1)$$

This and all other equations presented here are for the case where both the line source and the receptor are at ground-level. χ is the concentration,

q_ℓ is the emission rate, u is the wind speed, and σ_z is the dispersion parameter value dependent upon distance from the source and stability class. The distance from source to receptor is x. a is the virtual distance to give the required initial σ_z (discussed below).

Calder (1973) has given a modified equation to use when the line source can still be regarded as infinite in length but the wind deviates from the perpendicular. Deviations as much as 75° from the perpendicular can be handled in this way for very long line sources (about 15 to 20 km). The equation used is:

$$\chi = \sqrt{\frac{2}{\pi}} \frac{q_\ell}{\sin \alpha \; u \; \sigma_z(x + a)} \qquad (2)$$

where α is the angle between the wind direction and the orientation of the line source and x, which is the distance from the receptor to the point on the line source directly upwind, is found from:

$$x = d/\sin \alpha$$

where d is the perpendicular distance of the receptor from the line source. If more than one lane of a roadway is being simulated, the equation must be applied to each lane independently and the resulting concentrations summed.

When the wind direction is close to that of the line source, or the line source can no longer be regarded as infinite so that end effects may occur; Calder's approximation is no longer valid. The calculation of concentration must be made by a simple numerical integration of the Gaussian plume point source equation over a finite length. The coordinates of the end points of a line source of length L extending from point A to B (see figure 1) are R_A, S_A and R_B, S_B. The direction of the line source from A to B is β. The coordinates R, S of any point along the line at the arbitrary distance ℓ from point A is given by:

$$R = R_A + \ell \sin \beta$$

$$S = S_A + \ell \cos \beta$$

Given a receptor at R_k, S_k, the downwind distance, x, and the crosswind distance, y, of the receptor from the point R, S for any wind direction θ is given by:

$$x = (S - S_k) \cos \theta + (R - R_k) \sin \theta$$

$$y = (S - S_k) \sin \theta - (R - R_k) \cos \theta$$

Since R and S are functions of ℓ, x and y are also functions of ℓ.

The concentration, χ from the line source is then given by:

$$\chi = \frac{q}{u} \int_0^L \frac{\exp(-y^2/2\sigma_y)d\ell}{\pi\, \sigma_y(x+b)\sigma_z(x+a)}$$

where a and b are the virtual distances required to produce the initial σ_z and σ_y respectively.

The trapezoidal approximation to the integral is found by the following. Let $\Delta\ell = L/N$

$$\chi = \frac{q\Delta\ell}{u} \left[\frac{1}{2}(f_0+f_N) + \sum_{i=1}^{N-1} f_i \right] \tag{3}$$

where:

$$f_i = \frac{\exp\left\{ \dfrac{-y^2[i\Delta\ell]}{2\sigma_y^2(x[i\Delta\ell]+b)} \right\}}{\pi\, \sigma_y(x[i\Delta\ell]+b)\, \sigma_z(x[i\Delta\ell]+a)}$$

For a given initial choice of the interval length, $\Delta\ell$, the calculation is then interatively repeated with twice the number of intervals, that is, with $\Delta\ell/2$, $\Delta\ell/4$ ..., until the concentration estimates converge to within some specified limit of accuracy. This value then represents the true value of the integral.

Figure 2 gives guidance on which equation or procedure to use for receptors near a specific line source. For winds perpendicular to the source, equation (1) can be used over a wide area. Equation (2) can be used over a smaller area. The size of both of these areas increases with length of the line source. Also the angular range for which equation (2) applies, changes somewhat with source length.

The initial dispersion caused by the downwash or wake effect behind each individual vehicle is considered in the model by assuming an initial σ_y (horizontal dispersion parameter) value of 3 meters, and an initial σ_z (vertical dispersion parameter) value of 1.5 meters at each point along the line source. This is depicted in Figure 3.

SPECIFIC EXAMPLE

The example discussed here relates to particulate sulfate concentrations produced by automobiles. Most gasoline marketed in the United States contains a small amount of sulfur. In order to meet automobile emission standards for carbon monoxide and hydrocarbons, catalytic converters are scheduled for use on a number of 1975 model-year automobiles. The converter will oxidize carbon monoxide and hydrocarbons to water vapor and carbon dioxide. It will also oxidize the sulfur in the exhaust to sulfur trioxide which will rapidly convert to sulfuric acid due to the high humidity in the exhaust. Sulfuric acid mist and other sulfate aerosols will result.

Measurements of atmospheric sulfate have been related to adverse health effects in various studies (Finklea, 1973). It is therefore desirable to estimate sulfate particulate levels at receptor locations near busy roadways. Since associated health effects have been compared with 24-hour measured air quality levels, it is desirable to make the estimates with the model for up to 24 hours.

An estimate of emission rate of sulfate from catalytic equipped vehicles was first obtained from the mobile source air pollution control experts. Computations were then made on the assumption that 25% of the vehicle miles traveled on the roadway segment were by vehicles equipped with catalytic converters. A segment of expressway, 10 lanes in width, (43 meters wide including a 3 meter median) and 2 kilometers in length was chosen as the source. Traffic flow rate at the busiest time of day was assumed to be 2,000 vehicles per hour per lane.

Estimates of hourly concentrations were made for a day having rather typical meteorological conditions, and for a day with adverse meteorological conditions. Receptor locations, perpendicular to the mid point of the 2 km highway, were considered at 3, 50, and 500 meters away from the downwind edge of the highway. Computations were made with the wind perpendicular to the highway segment. Computations were then made varying the angle of wind direction to the highway in order to determine what angle produced the maximum concentration at each specific receptor. The results of these short term estimates with an everaging time of one hour are shown in Table 1.

Computations of 24-hour sulfate concentrations at each receptor were then made, varying both meteorological conditions and the volume of vehicles, hour by hour. Realistic vehicle flow rate variations were obtained from highway experts. The hourly meteorological conditions used were from a 24-hour period of airport data. This 24-hour period was selected for its light wind speeds, stable conditions, and small variability in wind direction. An orientation of the highway segment was chosen so that there was some cross-expressway component of the wind in the same direction during most of the 24 hours. The temporal variations in concentrations at the various receptors are shown in Figure 4. Average estimated 24-hour concentrations during this period at the receptor distances of 3, 50, and 500 meters are 11, 5, and 0.2 μgm^{-3}, respectively. Although this computation may not represent the worst situation, it can be considered as an adverse situation with regard to size of highway, amount of vehicular traffic, and meteorological conditions.

MODEL LIMITATIONS AND CONFIDENCE LIMITS

The application of the Gaussian line source model is restricted to cases where there is horizontal flow and a representative mean wind can be determined between the source and the receptor. The influence of local roughness which is caused by trees or buildings close to the roadway is not included in this model. It is assumed that the surroundings are nearly-level open country. The dispersion parameter values σ_y and σ_z, are basically extrapolations to shorter travel distances of the dispersion parameter values for the Pasquill stability types used in Workbook of Atmospheric Dispersion Estimates (Turner, 1970). Therefore, these may be slightly in error due to local roughness. The initial mixing zone due to the turbulence behind vehicles is estimated from a very limited amount of data and could be subject to change with availability of future field studies. Changing the stability classification by one class will change the concentrations by 10 to 20% close to the source and as much as a factor of 2 at distances greater than about 1 km. Including other sources of error, the accuracy of the model is that estimates might be expected to be within field measurements by a factor of 3 to 5.

There have been some limited comparisons of calculations with the model and field measurements. These comparisons have not been sufficient in number to validate the model with regard to the full range of stability classes or the entire range of possible angles of the wind with the roadway. The initial σ's and the dispersion parameter values themselves are subject to change in response to further field measurements and consideration of local surface roughness. The model should not be applied to highway locations on a fill or built upon elevated columns above the ground surface because in these situations the flow can not be considered horizontal.

MODEL SENSITIVITY

The model assumes concentrations are inversely proportional to wind speed. As mentioned previously, change of stability class will cause considerable changes in concentration. Figure 5 shows the concentrations at receptor locations downwind of the line source for various stability classes for the case of perpendicular winds. A four lane highway 19 meters wide with a 3 meter median was used for this exercise. The highway segment is 5 kilometers long with the receptors perpendicular to the center of the segment. So as to be normalized for the emissions and wind, emissions for each lane were assumed to be 1 g sec^{-1} m^{-1} and wind speed was set at 1 m sec^{-1}. Figure 6 shows the concentrations at receptor locations at the same distances from the identical line source but for wind direction only 10° from the orientation of the line source. Figure 7 shows the change in concentration as the angle of the wind with the source orientation changes for different receptor positions. The same source is used as for Figures 5 and 6. The stability used was class E. Note that for receptors close to the highway, the maximum concentration occurs with small angles of the wind to the source orientation. For receptors at greater distances from the source, the maximum concentration occurs with a larger angle. Although larger, these angles are still quite small, being only 17° from parallel with the line source for a receptor 500 meters from the source.

CONCLUSION

Line source models are useful for estimating concentrations from traffic on highway segments and airport taxiways and runways. A model based on the familiar Gaussian assumptions can be used for the full range of receptor locations and wind orientations with the line source for situations where the wind blows horizontally along the ground surface. These assumptions are most completely fulfilled for at-grade roadways with no significant obstructions to the flow at the side of the road. Although not completely validated for the full range of stability and wind angle situations, sufficient comparisons have been made with field measurements to give some degree of confidence in the use of this model. For more complex highway configurations other approaches such as the use of cellular models are in order.

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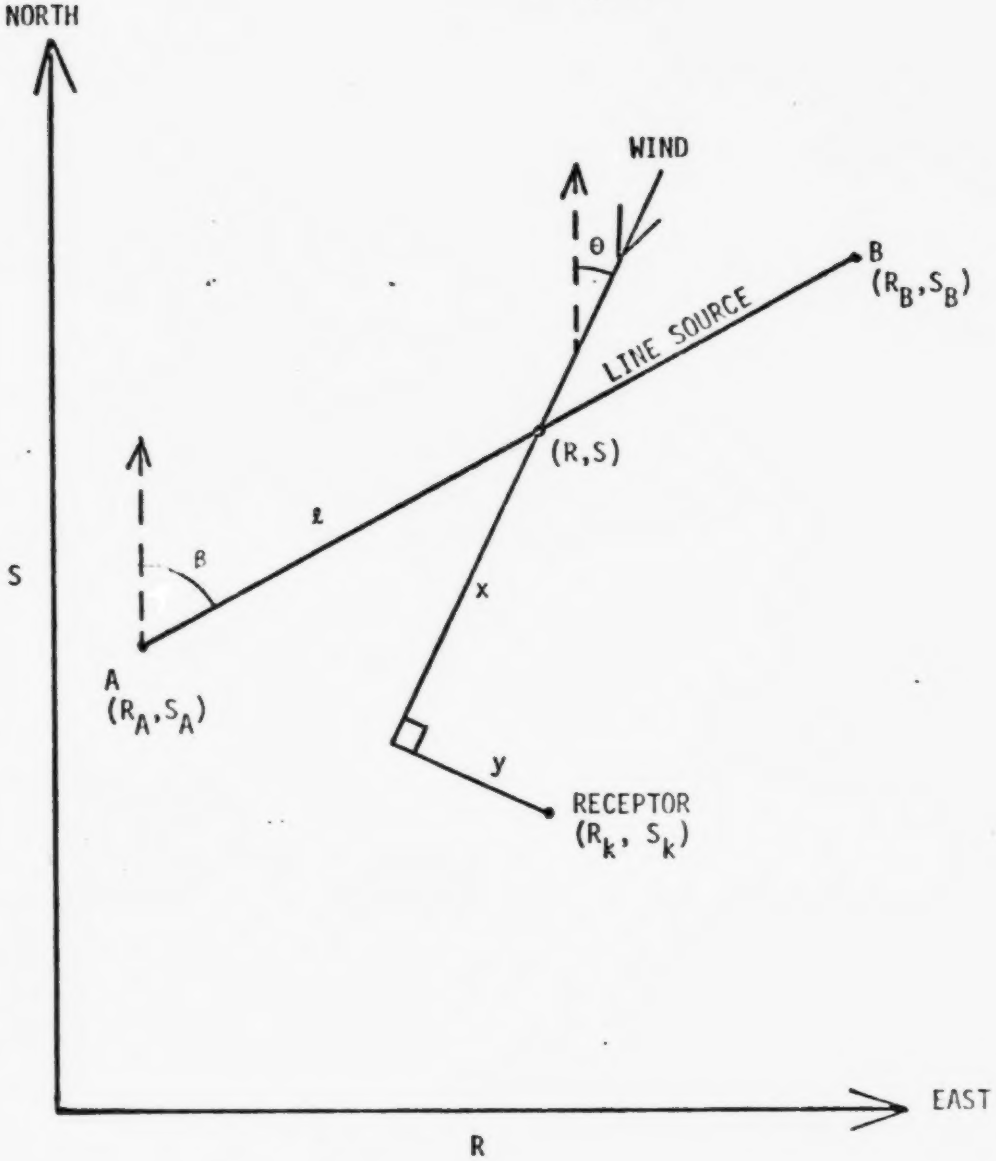
TABLE 1

ONE-HOUR ESTIMATED SUSPENDED PARTICULATE SULFATE AND SULFURIC ACID CONCENTRATIONS IN THE VICINITY OF A BUSY 10-LANE EXPRESSWAY.*

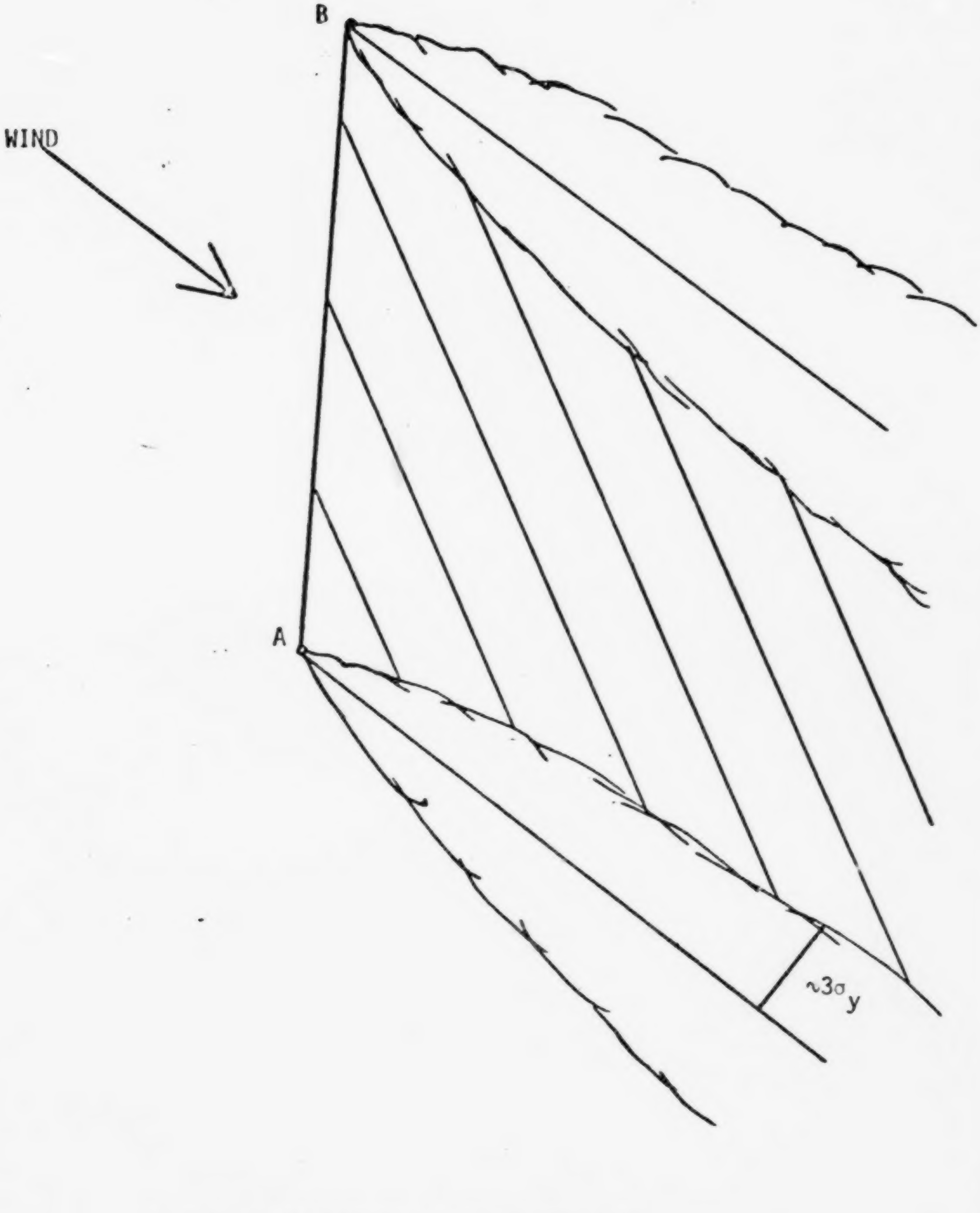
Distance from Edge of Expressway (meters)	Concentration ($\mu g\ m^{-3}$)			
	Normal Meteorology		Adverse Meteorology	
	Wind Perpendicular	Wind at Worst Angle	Wind Perpendicular	Wind at Worst Angle
3	2.1	5	20	88
50	1.3	2	19	33
500	0.3	0.3	5	6

* Assumes 25% of the vehicle miles traveled on a busy 10 lane expressway 2 km long (20,000 vehicles per hour at 30 mi hr^{-1}) are by vehicles equipped with oxidation catalyst devices emitting 0.05 grams of sulfuric acid or sulfate per vehicle mile. Other 75% of vehicle miles emit no sulfuric acid or sulfate.


NORTH
WIND
θ
B
(R_B, S_B)
LINE SOURCE
(R,S)
ℓ
β
S
x
A
(R_A, S_A)
y
RECEPTOR
(R_k, S_k)
EAST
R

LINE SOURCE AND RECEPTOR RELATIONSHIPS

FIGURE 1


B
WIND
A
$\sim 3\sigma_y$

EQUATION (2) CAN BE USED FOR THE AREA
WITH LINES BETWEEN THE PLUMES FROM THE
END POINTS..

ASSUMED INITIAL CONCENTRATION PROFILES IN THE HORIZONTAL AND VERTICAL RESULTING FROM INITIAL σ_y OF 3, AND INITIAL σ_z OF 1.5

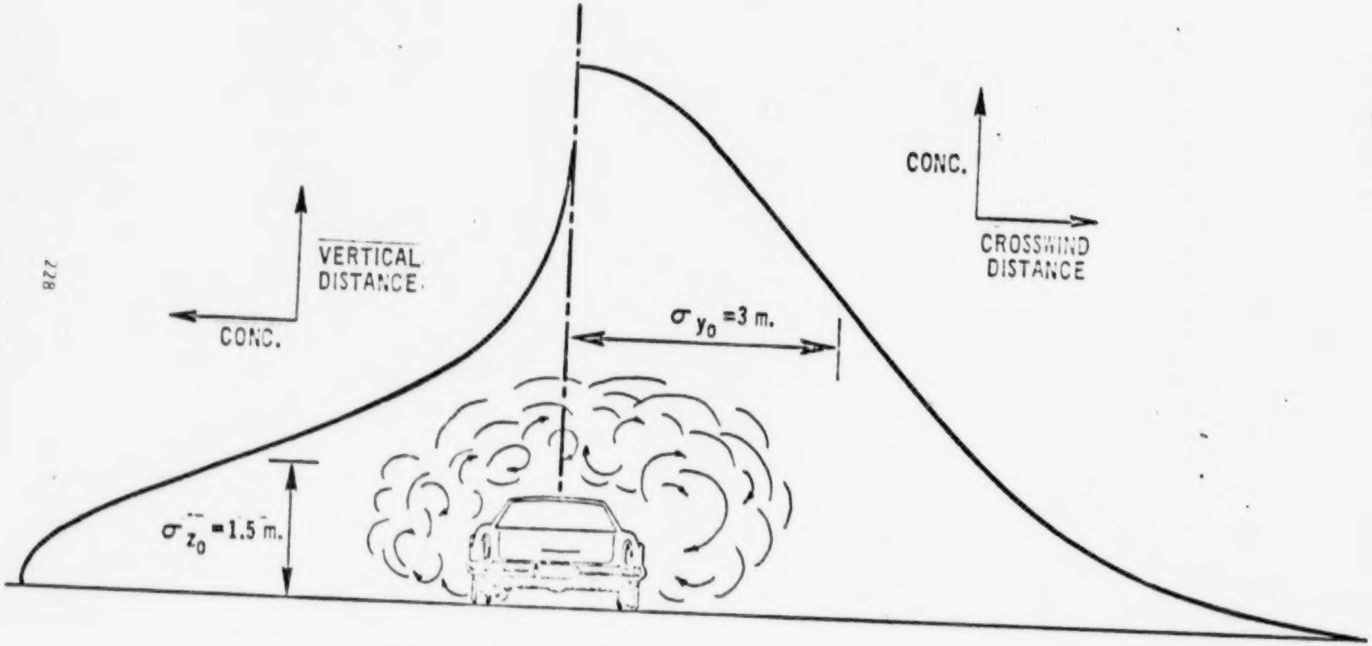

VERTICAL DISTANCE
CONC.
CONC.
CROSSWIND DISTANCE
$\sigma_{y_0} = 3$ m.
$\sigma_{z_0} = 1.5$ m.

FIGURE 3

ESTIMATED [illegible]
DURING 24 HOURS AT 3 DISTANCES FROM A HIGHWAY

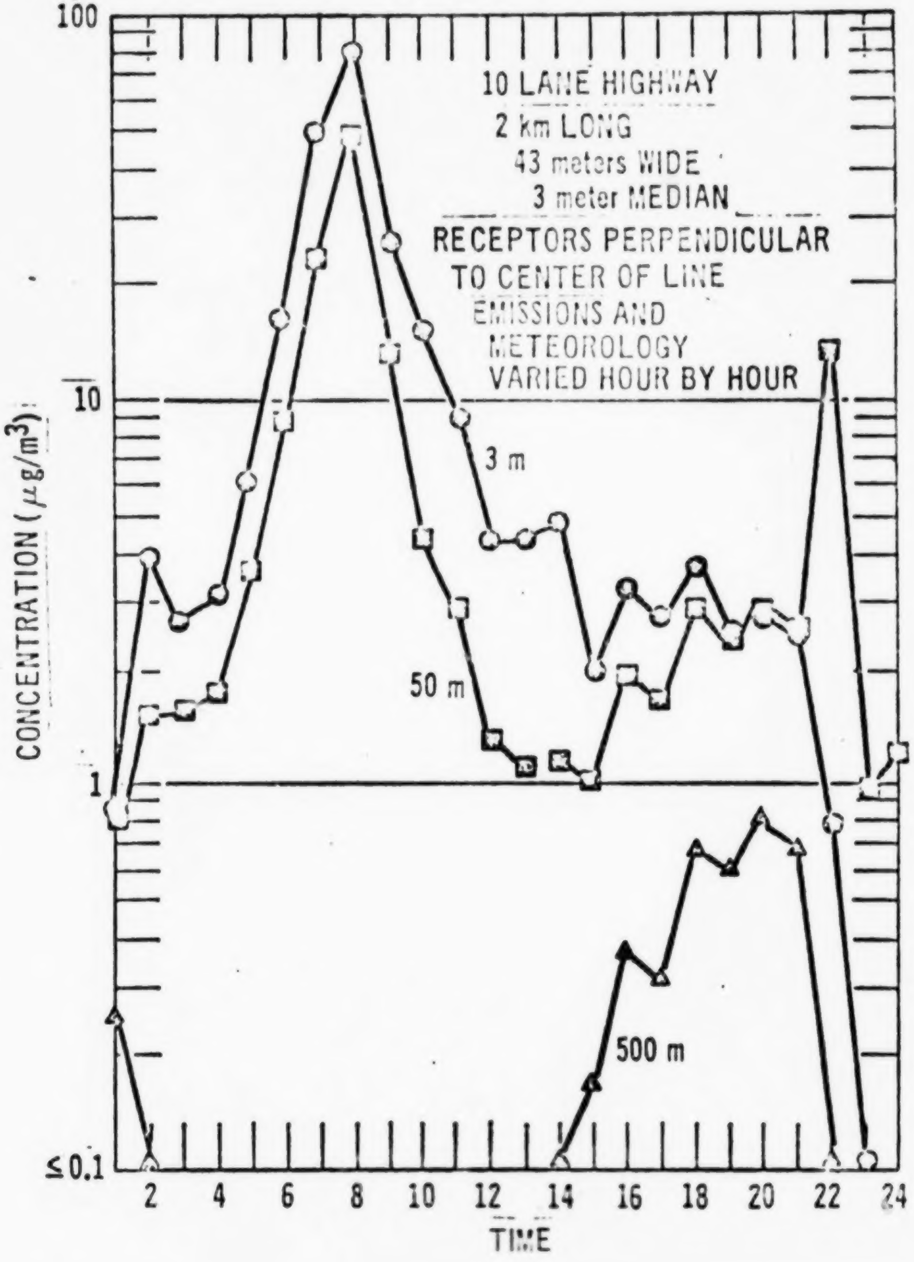


FIGURE 4

X AS A FUNCTION OF DISTANCE FROM ROAD FOR 6 STABILITY CLASSES
(PERPENDICULAR WINDS)

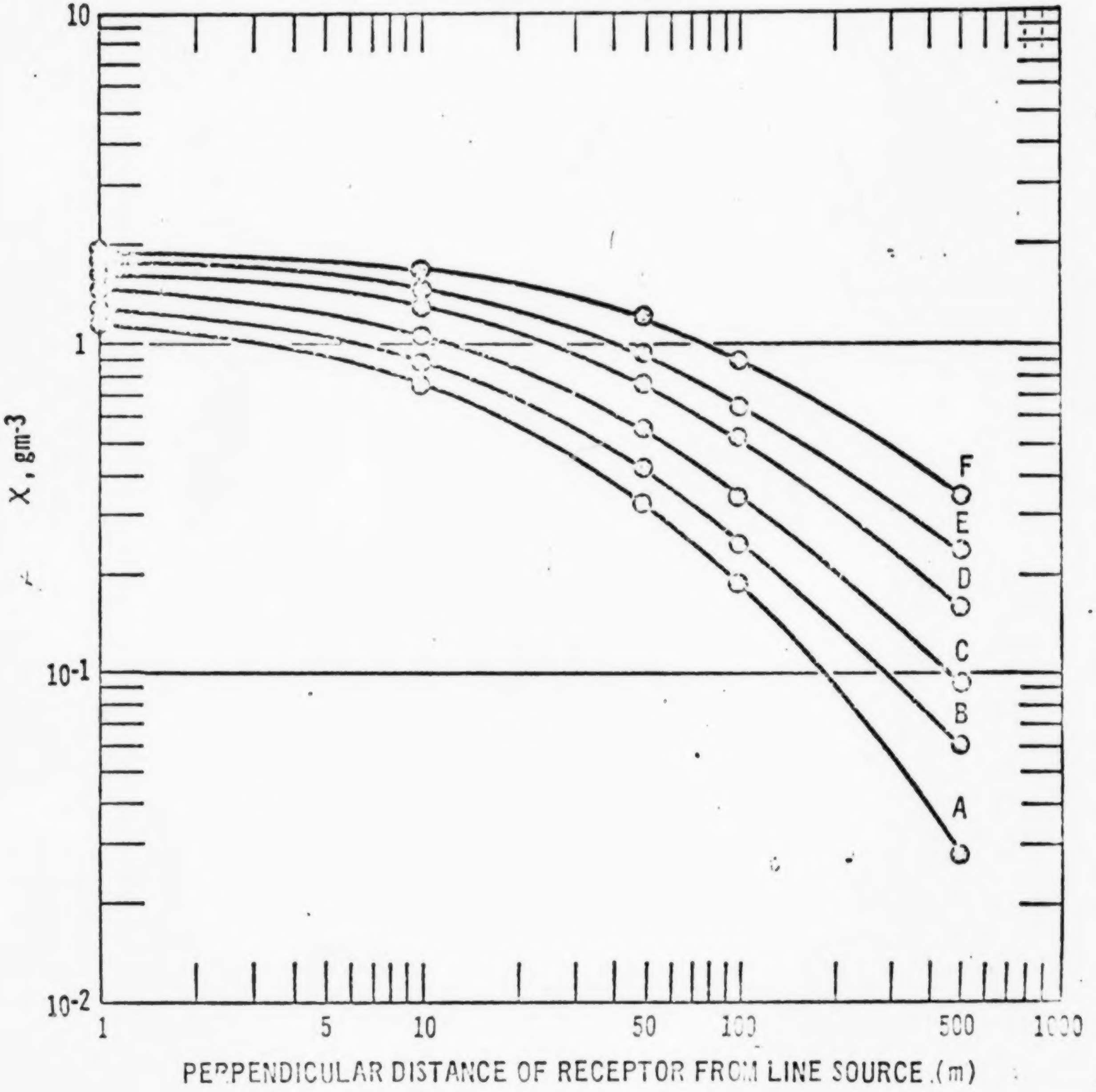
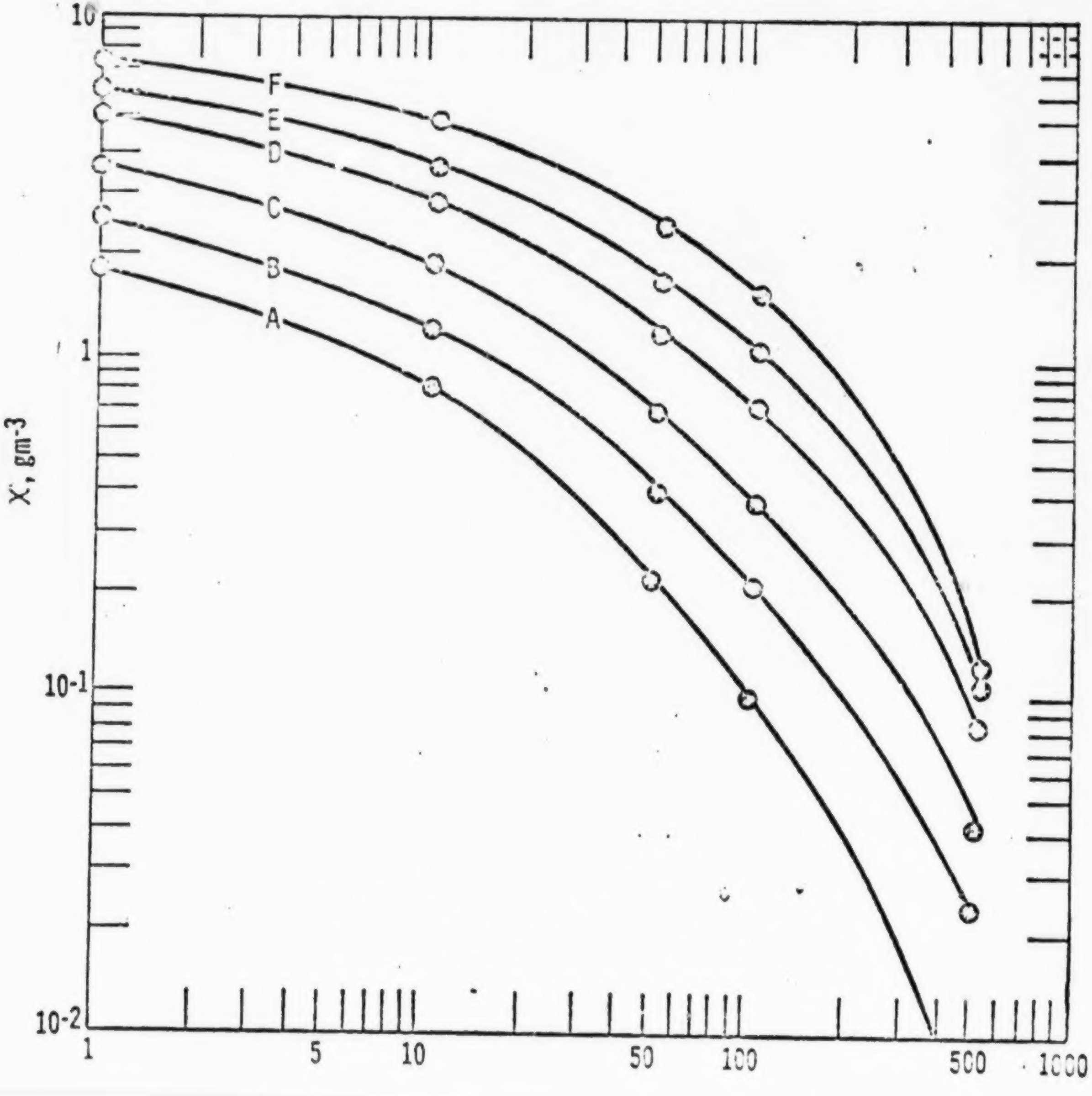


FIGURE 5

X AS A FUNCTION OF DISTANCE FROM ROAD FOR 6 STABILITY CLASSES
(WIND AT ANGLE OF 10° WITH LINE SOURCE)



χ AS A FUNCTION OF ANGLE OF THE WIND WITH LINE SOURCE
FOR 5 RECEPTOR DISTANCES

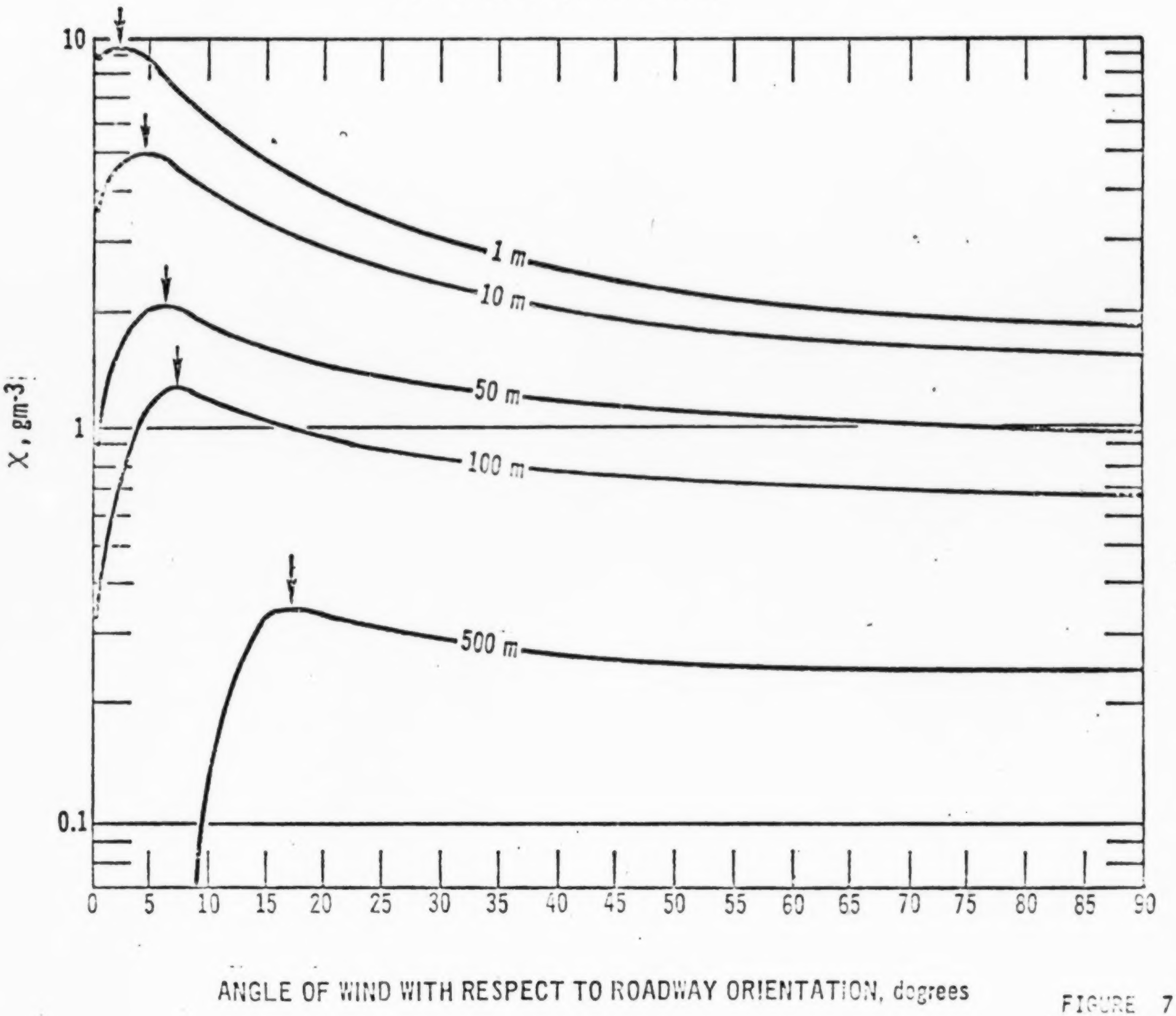


FIGURE 7

APPENDIX B7.1A

Status Report

Development of a Methodology to Determine the Effects of Fuel and Additives on Atmospheric Visibility

The initial work to study the effects of fuel and fuel additives on atmospheric visibility is being conducted by the Calspan Corporation. The Calspan Corporation contract is for a laboratory study to develop the measurement methodology and to use the recommended methodology for study of visibility reduction by emissions from automobiles using a "standard EPA fuel additive study reference fuel" and additives. The work is to be conducted in three phases: (1) methodology development (including test facility development), interim report on methodology development and recommendation, and (3) the application and methodology tests with automobiles using the reference fuel and the additives CI-2 and F-319.

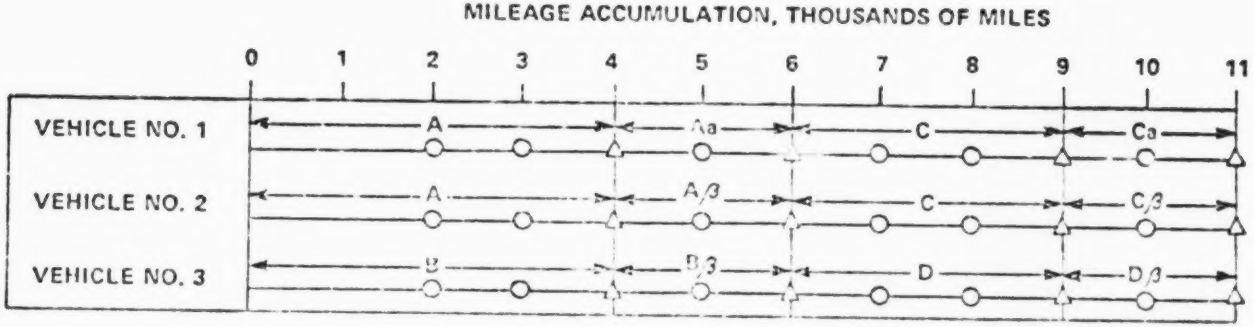
The test facilities for the study have been completed, the methodology development tests have been completed (phase 1), and an oral interim report recommending the measurement method has been presented (phase 2).

The results of the methodology tests indicate that the atmospheric visibility-reducing potential of exhaust emissions is primarily dependent on the HC/NO_x ratio of the emissions. The combustion products with the highest HC/NO_x ratio produce the most visibility reduction.

At present, a contract overrun is being negotiated for completing the third phase work. The overrun was due to unexpected delays in preparation of facilities for the study, slow stabilization of vehicle performance, and the lengthy sample test periods of 24 hours.

During the phase 3 part of the program, the exhaust emissions from a 1971 catalyst-equipped Ford automobile will be tested to determine the effect of the catalyst on the visibility effects of the emissions.

FIGURE 1 : ORIGINAL VEHICLE EMISSION TEST SCHEDULE


MILEAGE ACCUMULATION, THOUSANDS OF MILES
0
1
2
3
4
5
6
7
8
9
10
11
VEHICLE NO. 1
A
Aα
C
Cα
VEHICLE NO. 2
A
Aβ
C
Cβ
VEHICLE NO. 3
B
Bβ
D
Dβ

LEGEND

1. ○ = MILEAGE CONDITIONING TEST (SINGLE TEST)

2. Δ = REPRODUCIBILITY DEMONSTRATION TESTS (TRIPLICATE TESTS)

3. A = ENDOLENE 0
   B = ENDOLENE 0 + 0.5 GM/GAL TEL
   C = EPA REFERENCE FUEL
   D = EPA REFERENCE FUEL + 0.5 GM/GAL TEL

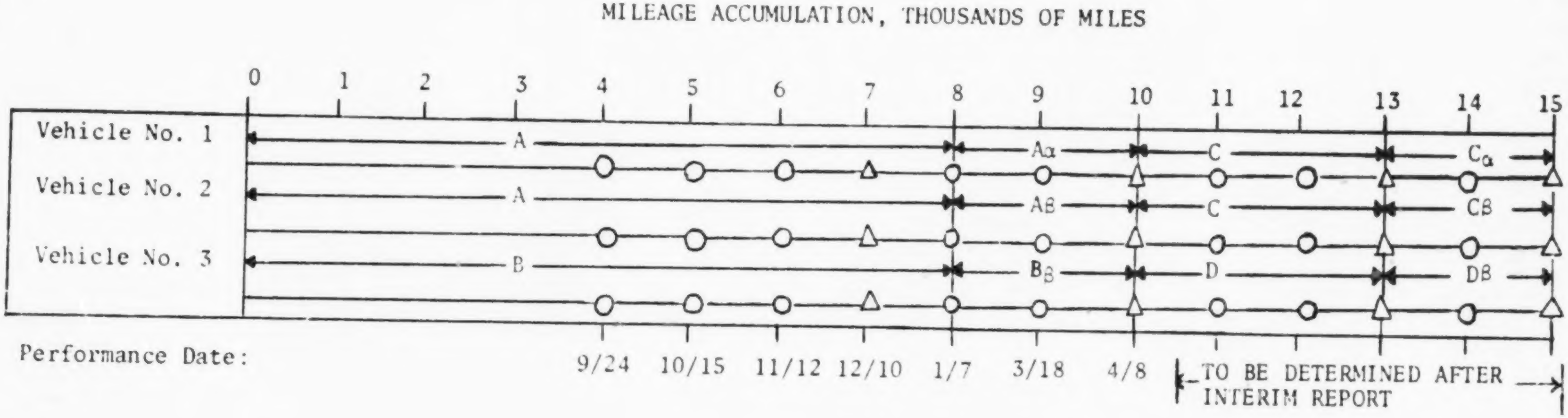
4. α = CHEVRON F-310
   β = ETHYL CI-2

NOTES:

1. AN UNSPECIFIED NUMBER OF PRELIMINARY TESTS WILL BE PERFORMED DURING THE FIRST TWO THOUSAND MILES

2. EACH ENGINE WILL BE CLEANED AND A NEW EXHAUST SYSTEM INSTALLED AFTER THE FIRST SIX THOUSAND MILES.

FIGURE 2 REVISED VEHICLE EMISSION TEST SCHEDULE



LEGEND

1. ○ = MILEAGE CONDITIONING TEST (SINGLE TEST)
2. Δ = REPRODUCIBILITY DEMONSTRATION TESTS (TRIPLICATE TESTS)
3. A = INDOLENE 0
   B = INDOLENE 0 + 0.5 GM/GAL TEL
   C = EPA REFERENCE FUEL
   D = EPA REFERENCE FUEL + 0.5 GM/GAL TEL
4. α = CHEVRON F-310
   β = ETHYL CI-2

NOTES:

1. AN UNSPECIFIED NUMBER OF PRELIMINARY TESTS WILL BE PERFORMED DURING THE FIRST SEVEN THOUSAND MILES
2. EACH ENGINE WILL BE CLEANED AND A NEW EXHAUST SYSTEM INSTALLED AFTER THE FIRST TEN THOUSAND MILES.

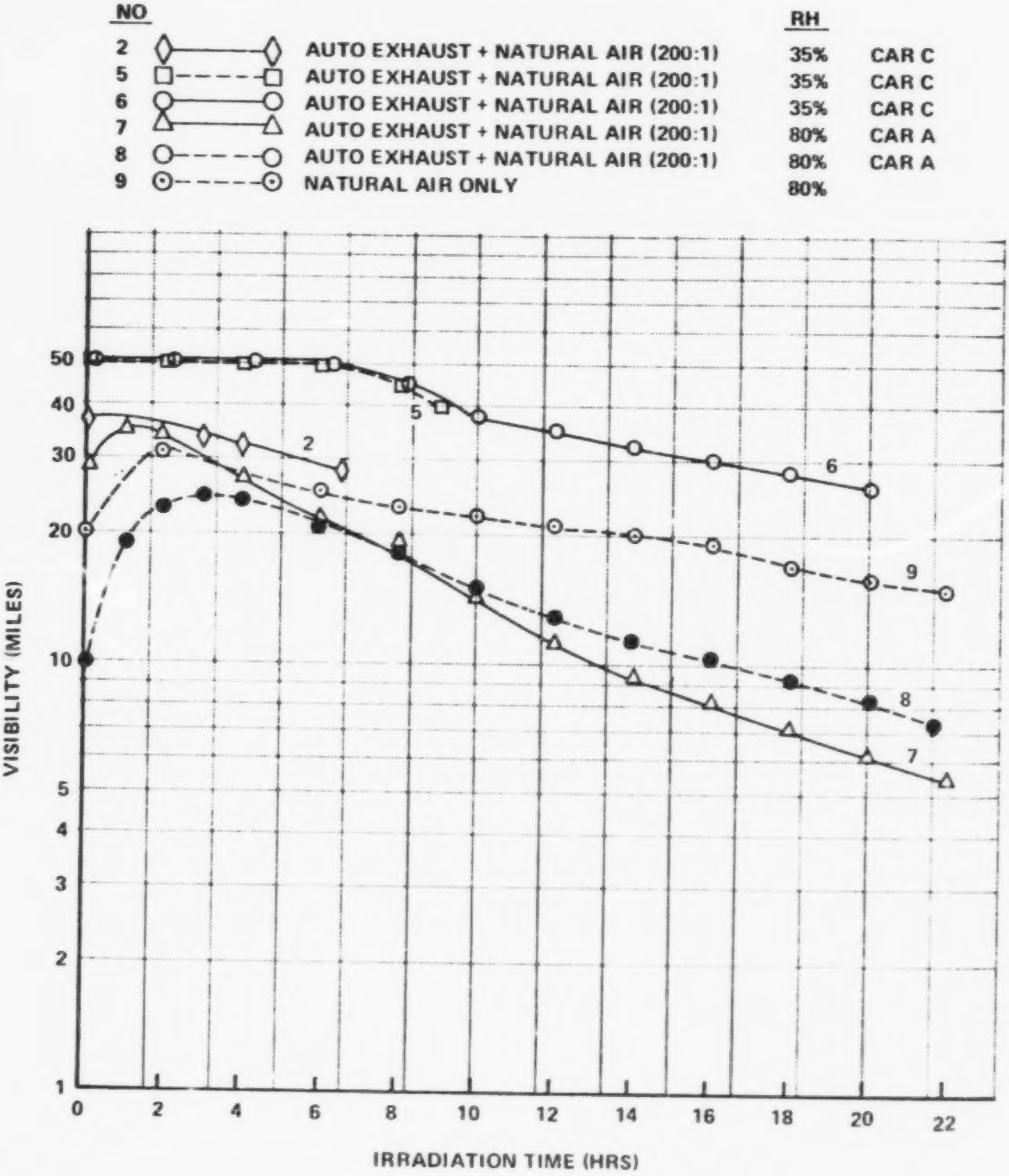


Figure 3 EFFECT OF VARIATIONS IN NATURAL AIR ON TEST RESULTS

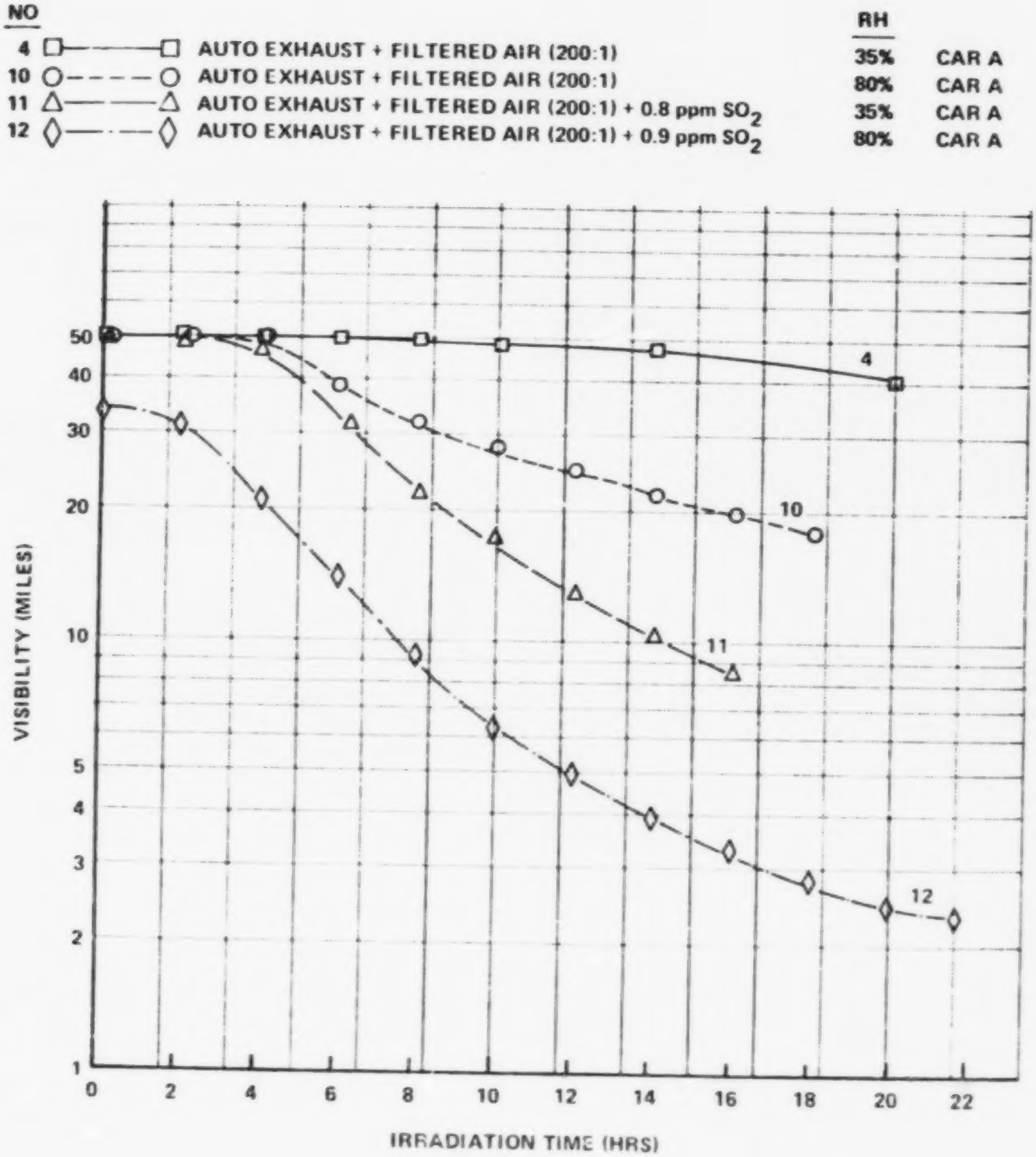


Figure 4 EFFECT OF RELATIVE HUMIDITY AND ADDED SO_2 ON TEST RESULTS

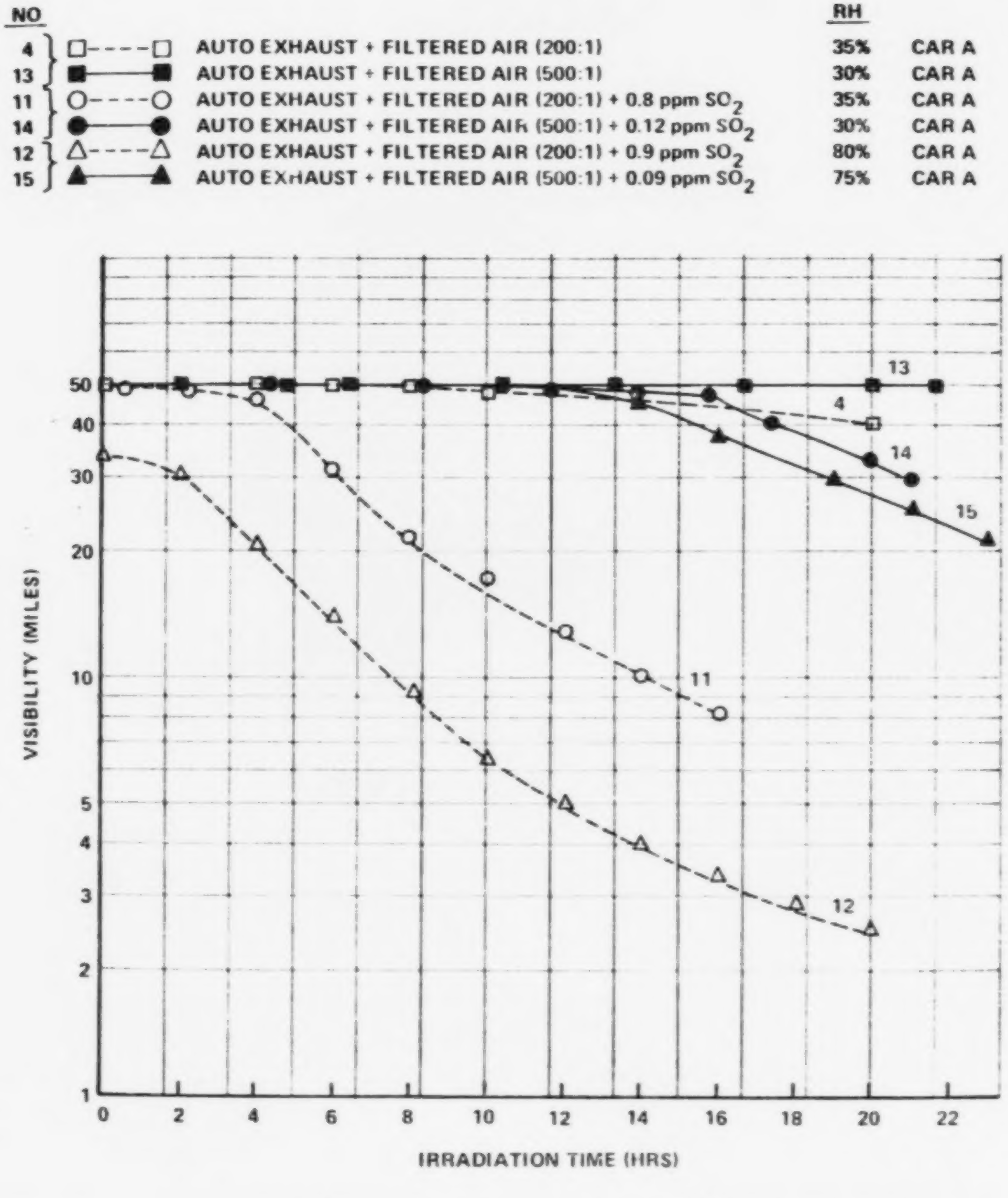


Figure 5 EFFECT OF DILUTION RATIO , RELATIVE HUMIDITY AND ADDED SO_2 ON TEST RESULTS.

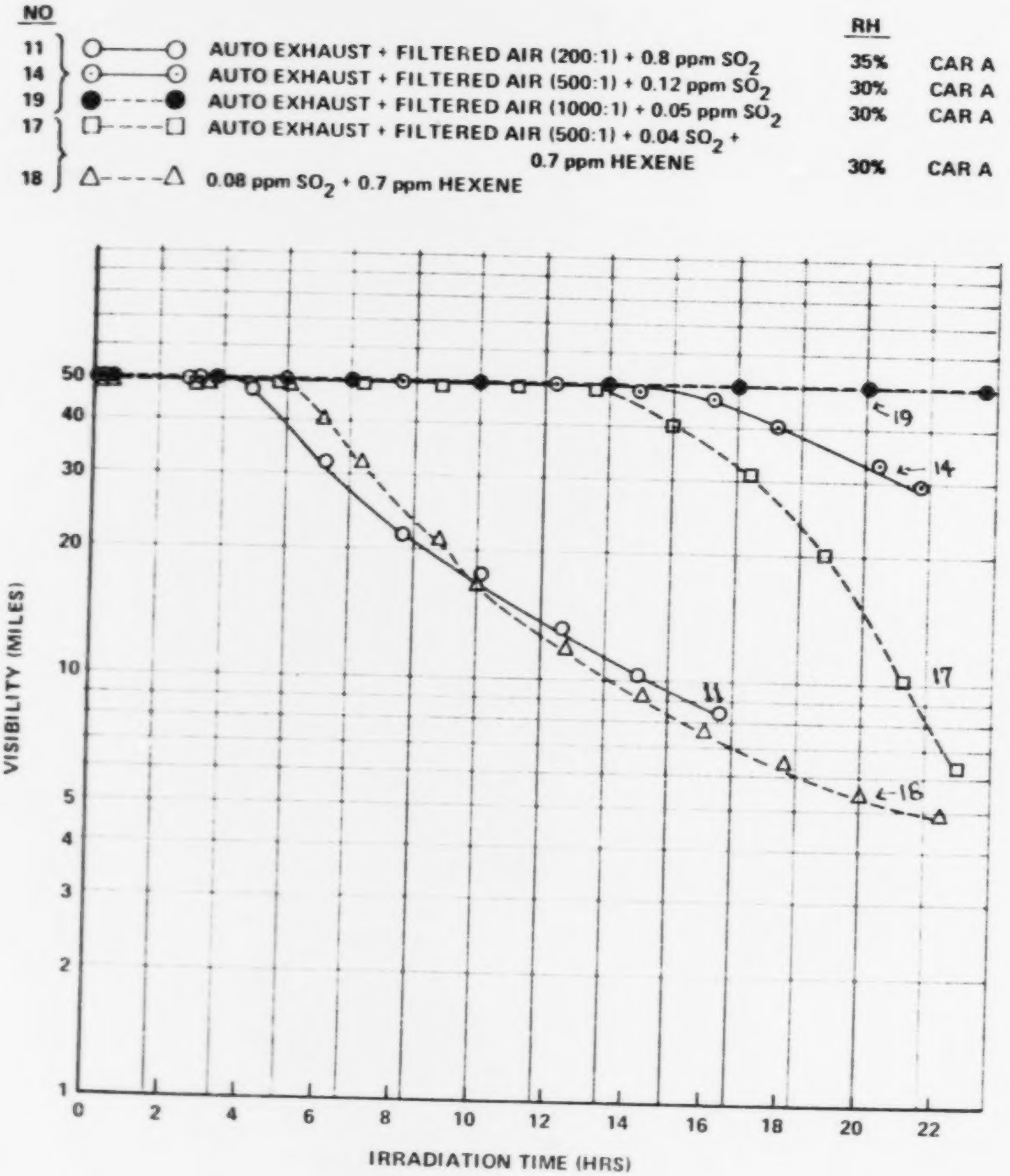


Figure 6 EFFECT OF DILUTION RATIO, ADDED HYDROCARBON AND SO_2 ON TEST RESULTS

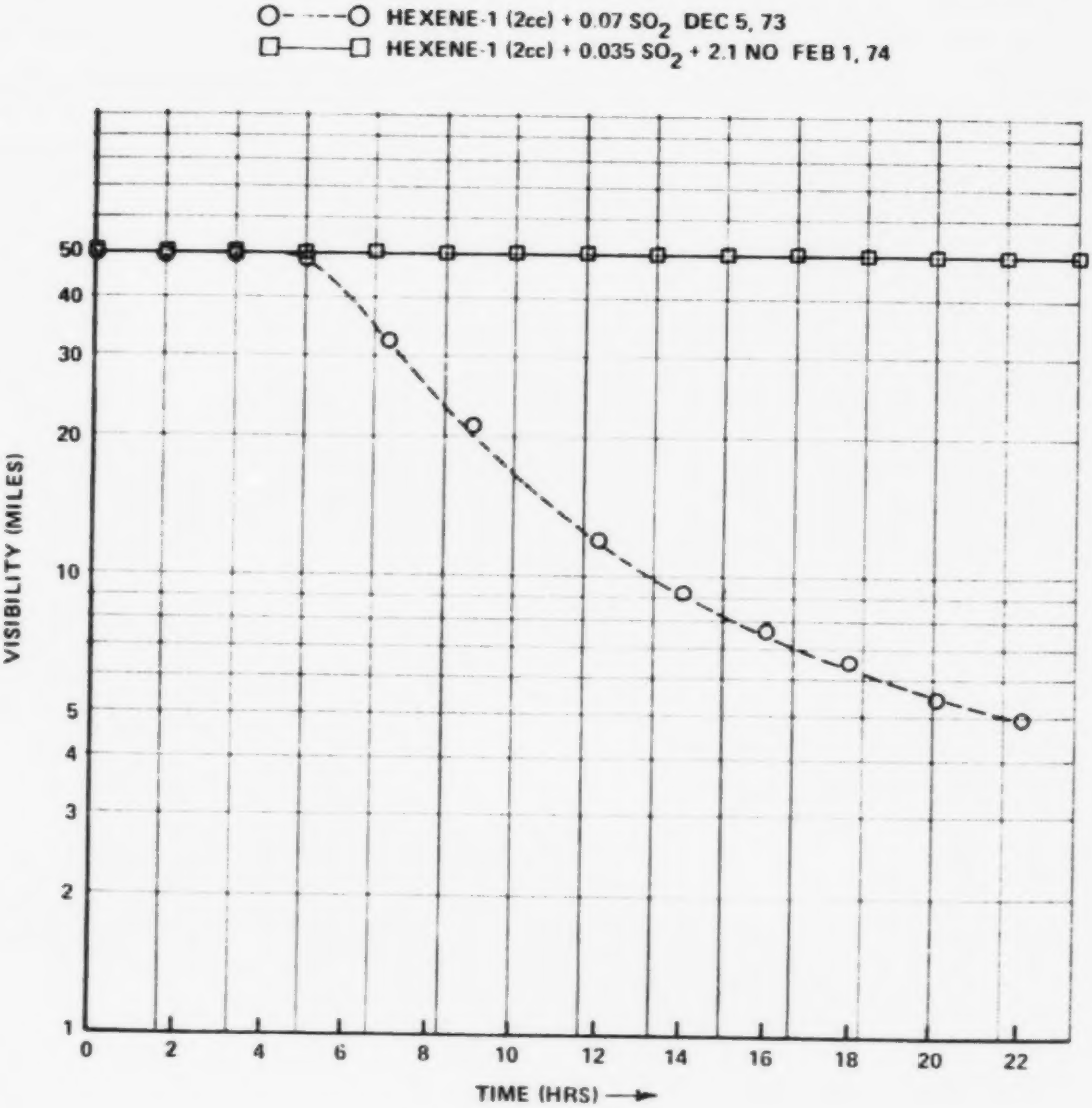


Figure 7 COMPARISON OF HEXENE-1•SO_2 IRRADIATION WITH AND WITHOUT THE ADDITION OF NO

TABLE I

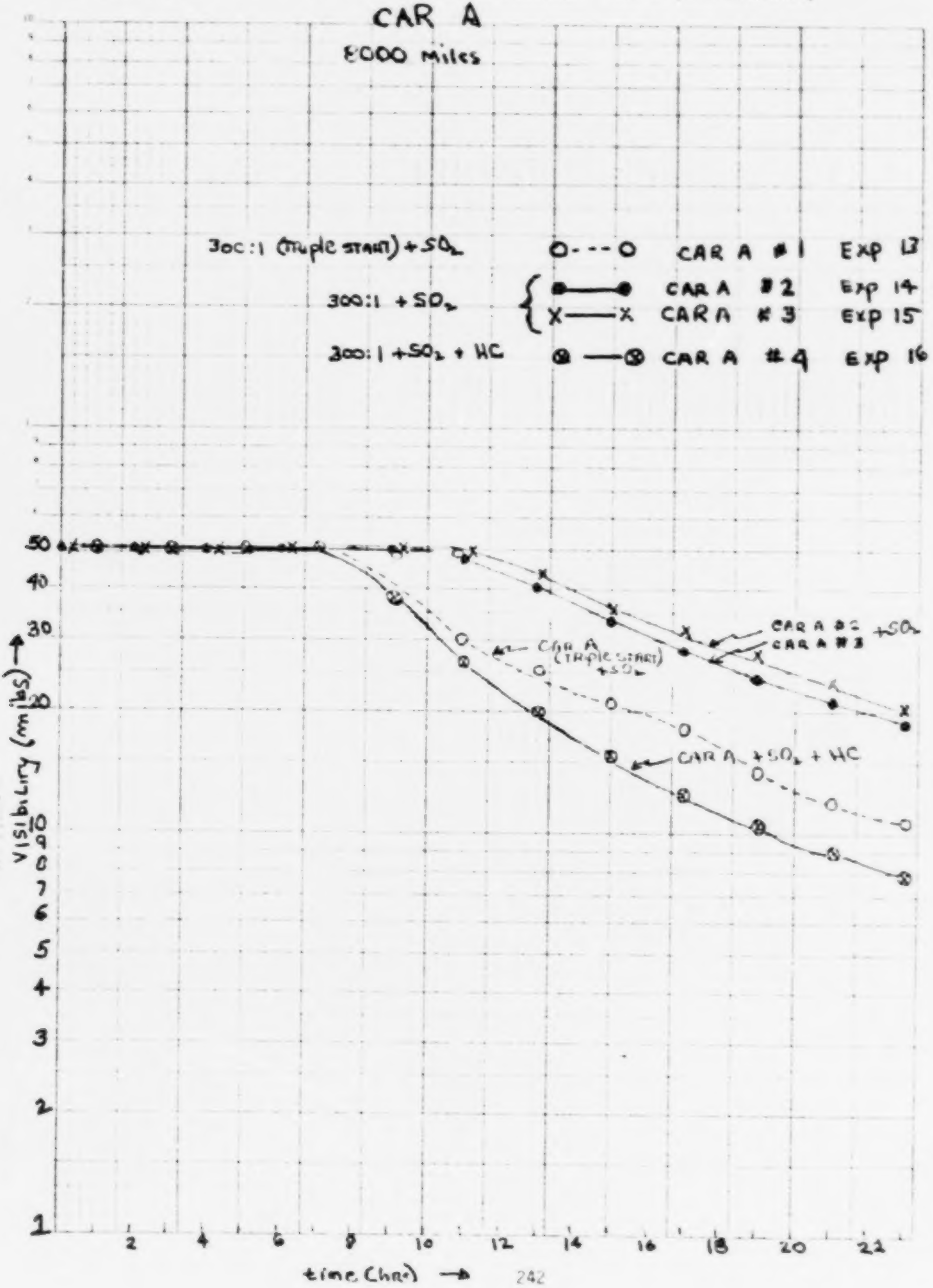
METHODOLOGY REPEATABILITY TESTS - CARS A, B & C

TEST	CONDITION*	T	RH	NO_i	NO_f	VIZ after 23 hrs	
Car A #1	300:1 + 0.05 SO_2	72°	33%	3.53	1.92	10.7	Engine Failure
Car A #2	300:1 + 0.05 SO_2	78°	25%	3.90	1.68	18.5	19.2 ±1.3
Car A #3	300:1 + 0.05 SO_2	80°	>22%	3.87	1.64	20.5	
Car A #4	300:1 + 0.05 SO_2 + 3 cc HC	79°	26%	3.65	1.90	7.9	
Car B #1	300:1 + 0.05 SO_2	65°	28%	3.50	1.56	19.0	20.8 ±2.0
Car B #2	300:1 + 0.05 SO_2	73°	29%	3.55	--	22.8	
Car B #3	300:1 + 0.05 SO_2	70°	28%	3.46	1.20	20.5	
Car B #4	300:1 + 0.05 SO_2 + 3 cc HC	74°	26%	3.72	1.02	8.0	
Car C #1	300:1 + 0.05 SO_2	72°	23%	3.58	1.40	17.5	16.5 ±2.5
Car C #2	300:1 + 0.05 SO_2	70°	27%	3.42	1.60	18.0	
Car C #3	300:1 + 0.05 SO_2	70°	28%	3.46	1.76	14.0	
Car C #4	300:1 + 0.05 SO_2 + 3 cc HC	70°	28%	3.70	2.12	3.4	

*All test samples irradiated for 23 hrs

For all non-lead tests (i.e., Car A + Car B) avg visibility = 20.3 ±2.2 mi

FIGURE 8 REPEATABILITY TESTS FOR 300:1 DILUTION – CAR A (NON-LEAD GAS)



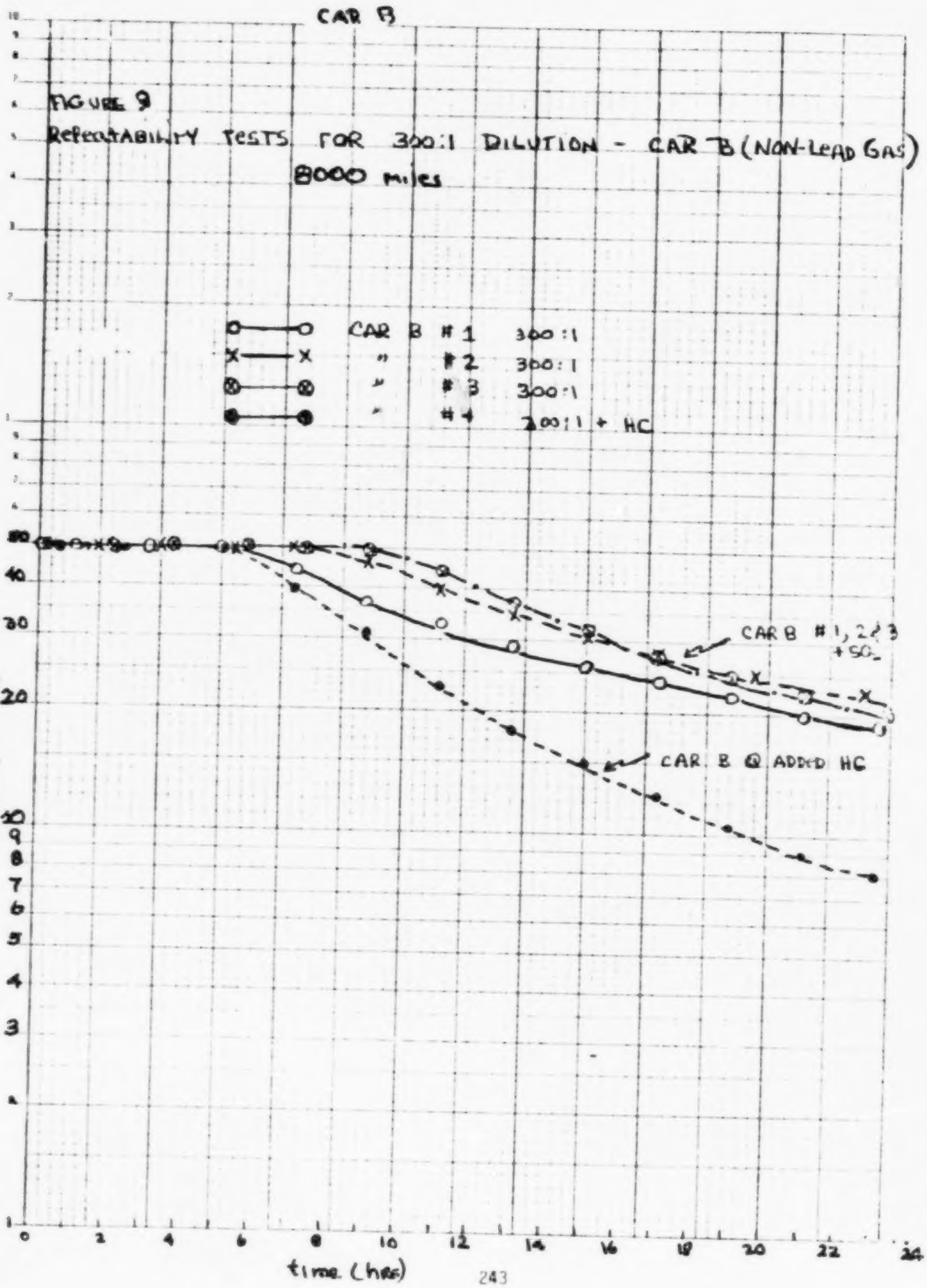
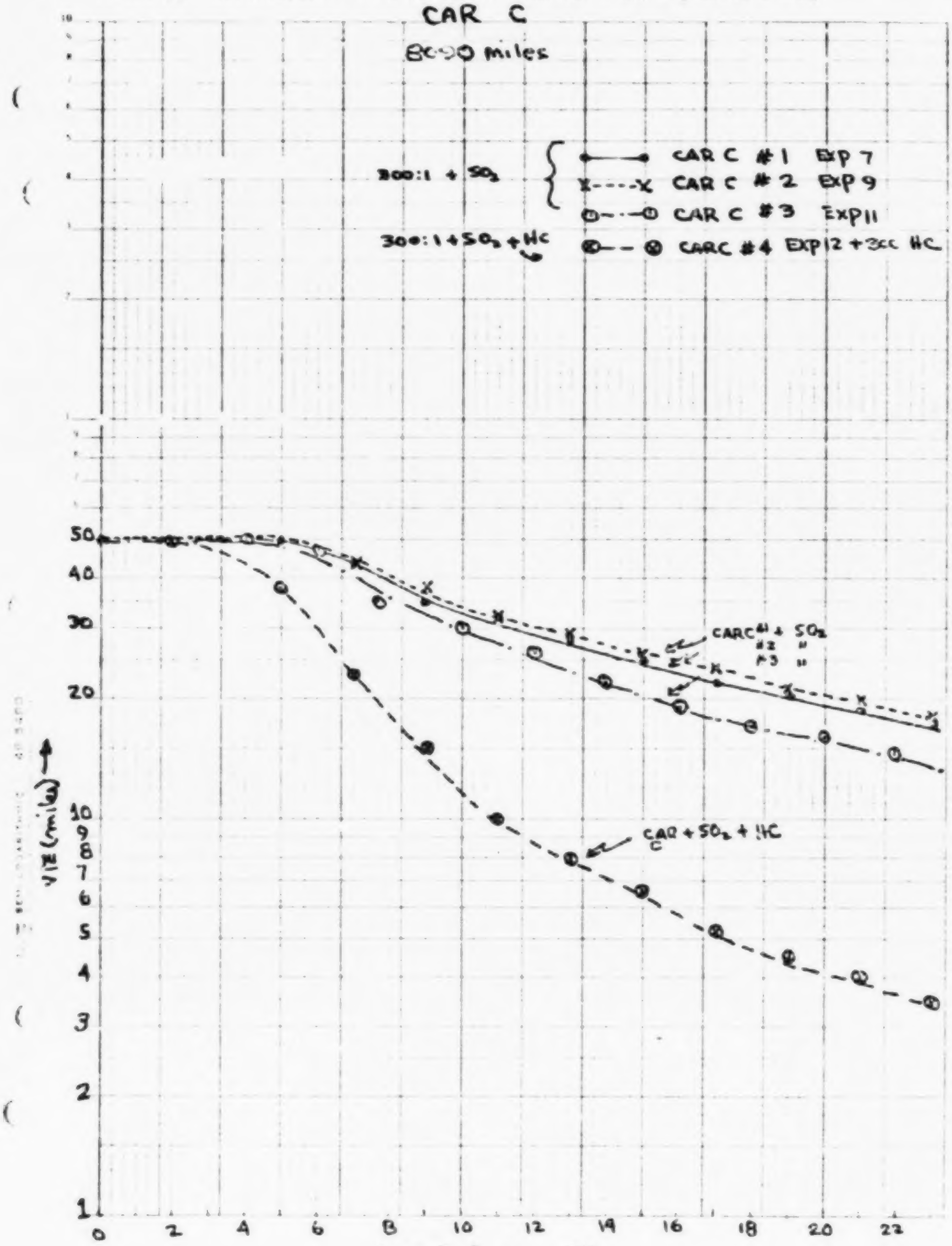


FIGURE 9

REPEATABILITY TESTS FOR 300:1 DILUTION - CAR B (NON-LEAD GAS)

8000 miles

FIGURE (1) REPEATABILITY TESTS FOR 300:1 DILUTION - CAR C (LOW-LEAD GAS)



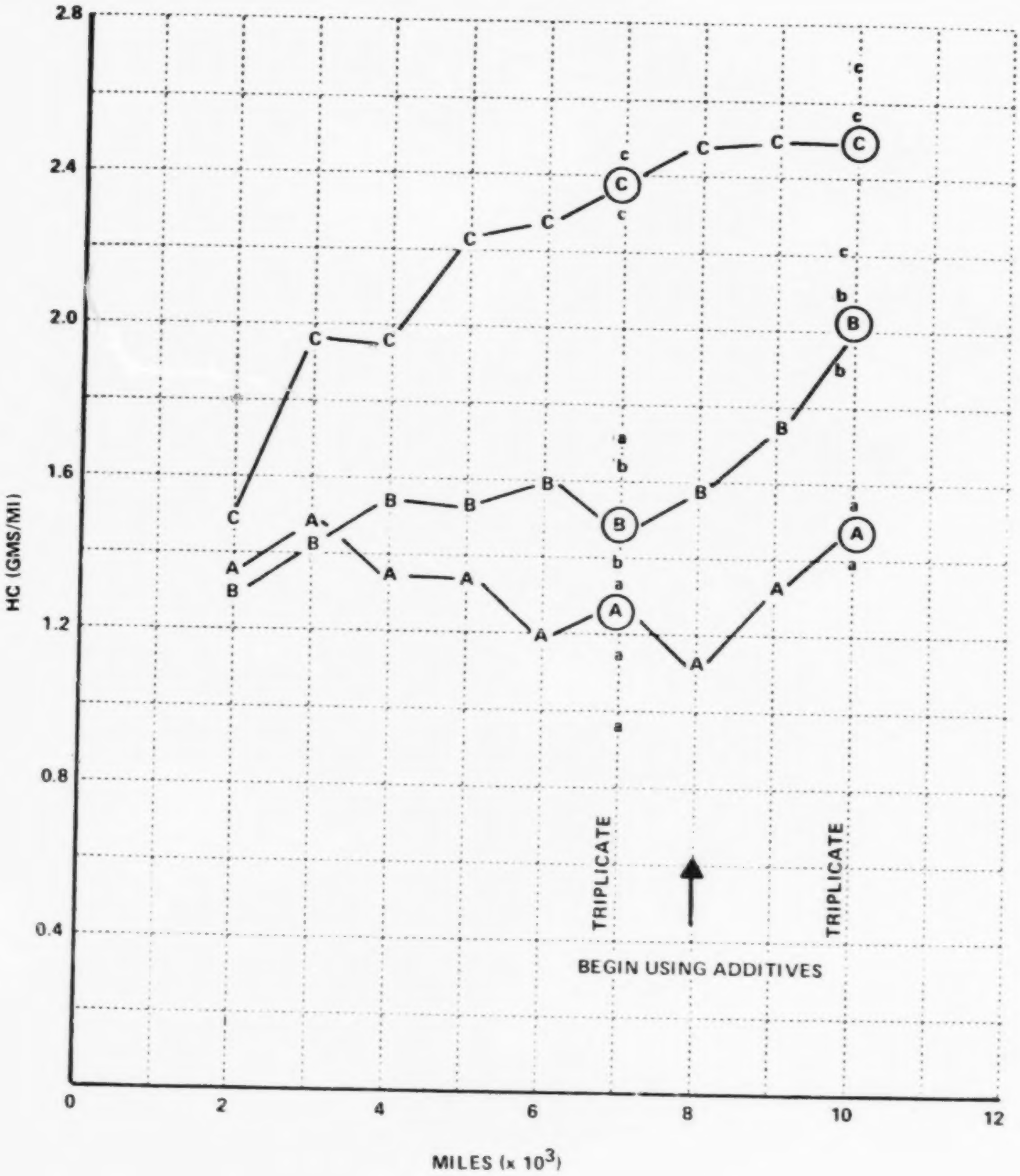


Figure 11 HYDROCARBON EMISSIONS VS MILEAGE ACCUMULATION

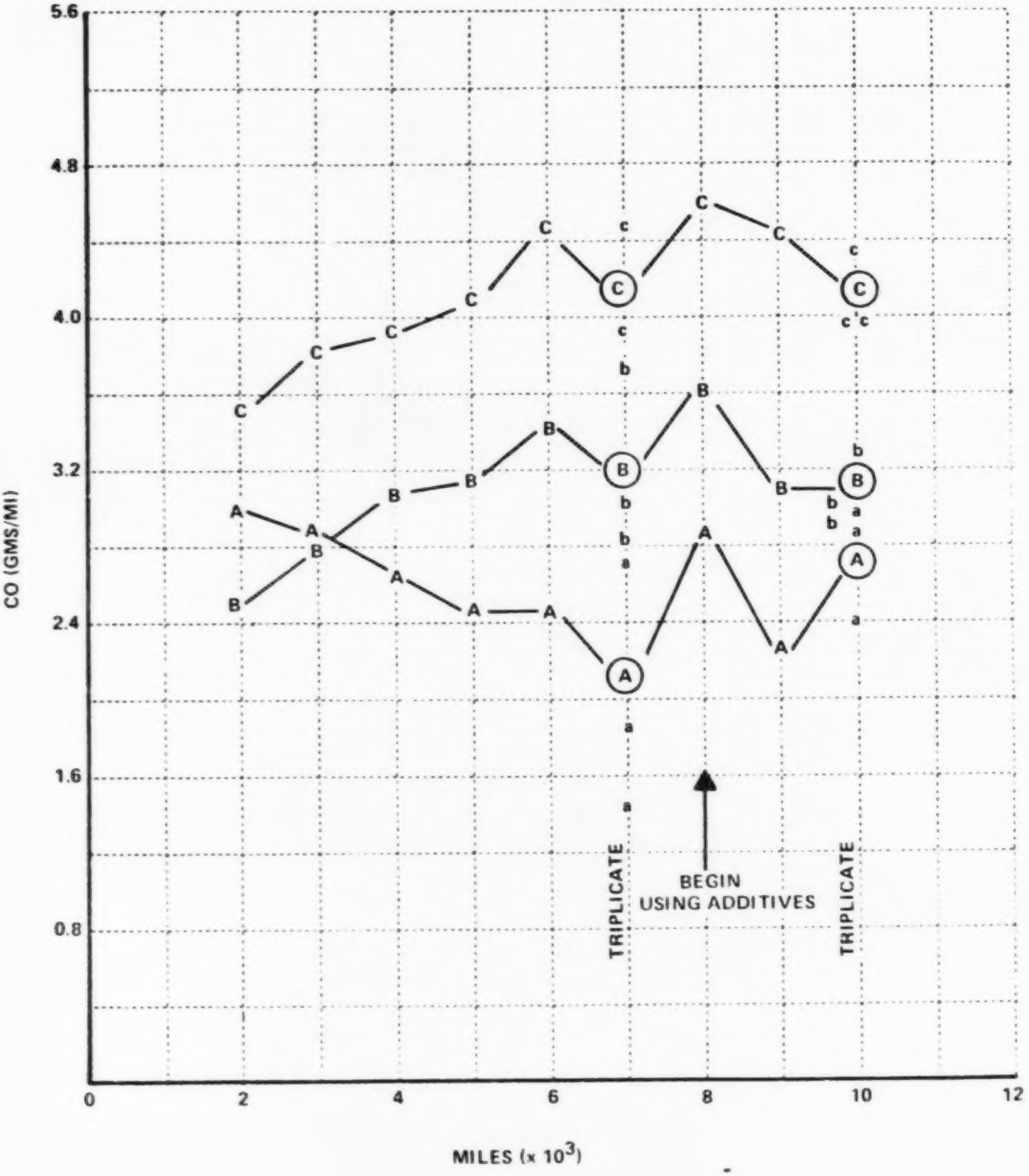


Figure 12. CARBON MONOXIDE EMISSIONS VS MILEAGE ACCUMULATION

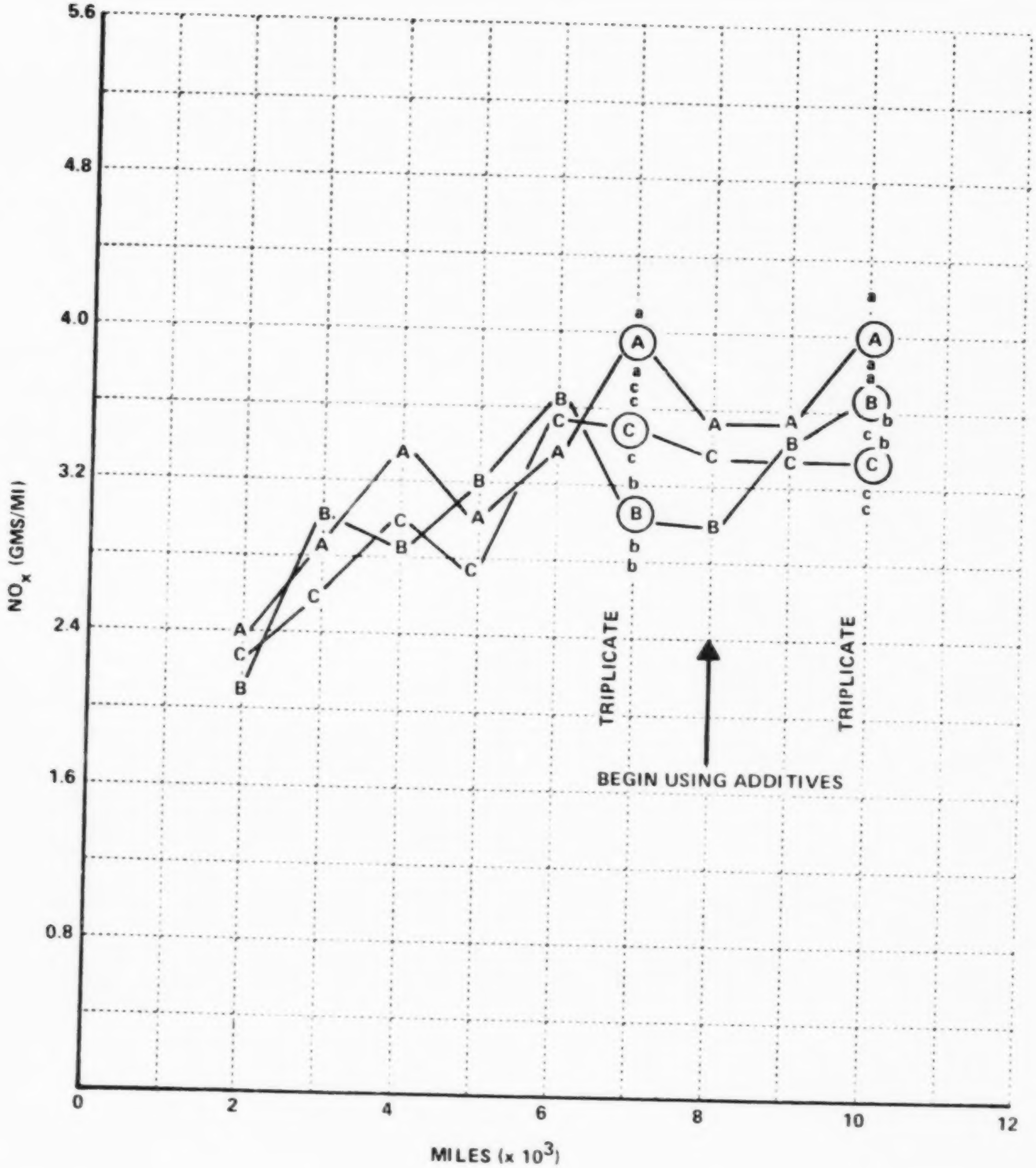


Figure 13 NO$_x$ EMISSIONS VS MILEAGE ACCUMULATION

TABLE I.

METHODOLOGY REPEATABILITY TESTS - CARS A, B & C

Test		Condition	T °F	RH %	NO_i ppm	NO_f ppm	HC ppmC	HC/NO_x	Visibility in miles after 23 hours irradiation April (10,000 mi)		Feb. (8000 mi)	
Car A	#18	300:1 + 0.05 SO_2	78	46%	2.94	1.30	3.15	1.07	21.8	26.4 ±12	10.7	
	#19	"	77	32%	4.10	2.20	2.50	0.61	38.0		18.5	19.2±1.3
non-	#20	"	77	41%	3.78	1.90	2.95	0.79	29.0		20.5	
lead	#21	"	79	55%	2.91	1.21	3.30	1.13	17.0			
fuel	#22	300:1 + 0.05 SO_2	80	43%	3.58	1.28	8.05	2.25	7.0		7.9	
+		+ 3 cc HC										
F-310												
Car B	#11	300:1 + 0.05 SO_2	67	39%	3.45	1.64	3.60	1.04	21.8	19.8 ±3.1	19.0	20.8 ±2.0
	#13	"	71	31%	3.55	1.78	3.55	0.97	22.9		22.8	
non-	#15	"	74	40%	3.47	1.62	3.90	1.13	16.8		20.5	
lead	#16	"	80	36%	3.30	1.35	3.75	1.13	17.8			
fuel	#17	300:1 + 0.05 SO_2	78	40%	3.27	0.90	8.85	2.70	6.0		8.0	
+		+ 3 cc HC										
CI-2												
Car C	#23	300:1 + 0.05 SO_2	70	36%	3.68	1.57	5.25	1.43	9.4	8.9 ±1.2	17.5	16.5 ±2.5
	#24	"	75	48%	3.20	1.13	5.25	1.64	7.7		18.0	
low-	#25	"	76	49%	3.32	1.29	5.00	1.51	9.8		14.0	
lead	#26	300:1 + 0.05 SO_2	83	51%	2.97	--	10.8	3.63	3.5			
fuel		+ 3 cc HC										
+ CI-2												

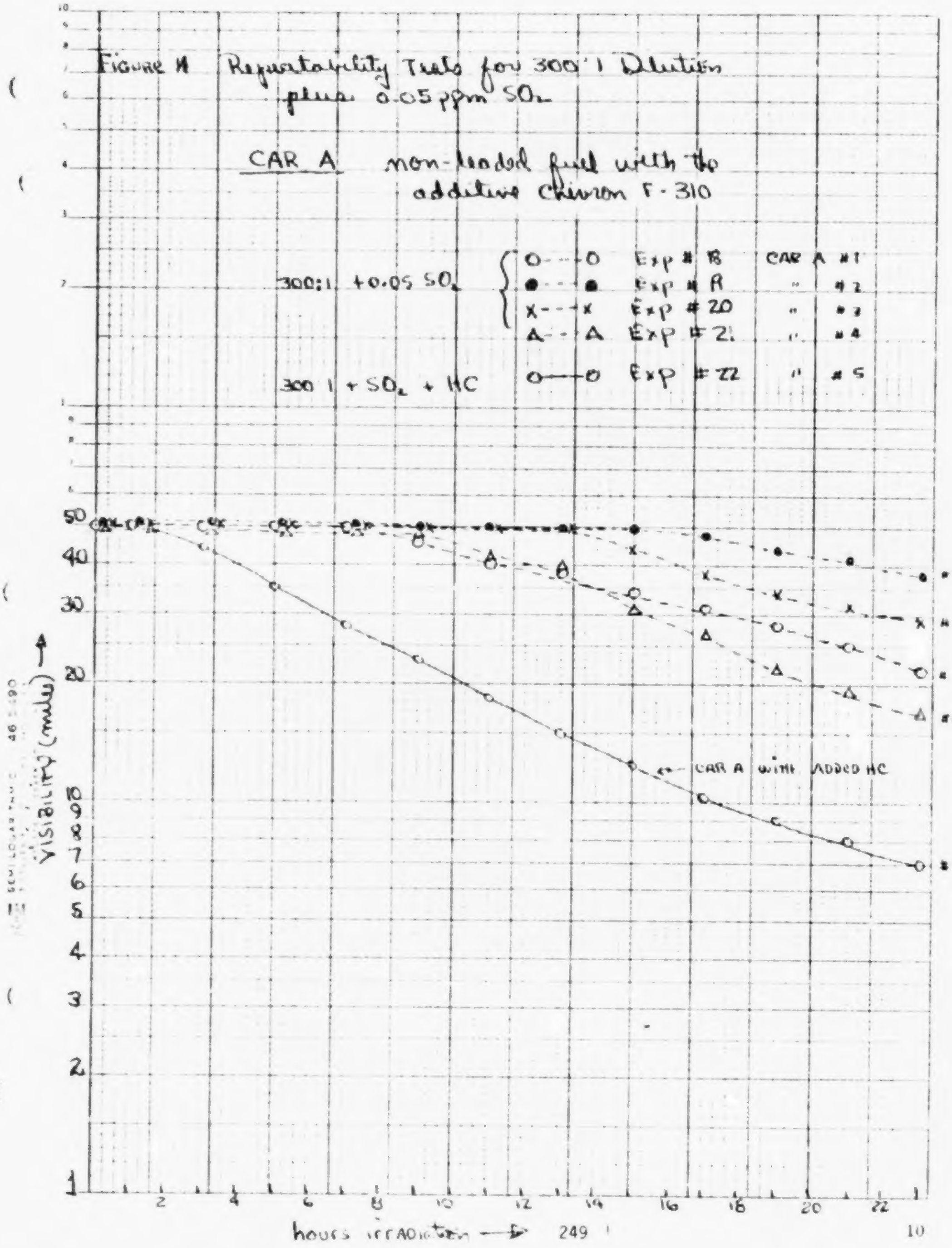


FIGURE 11 Repeatability Tests for 300:1 Dilution plus 0.05 ppm SO_2

CAR A non-leaded fuel with the additive Chevron F-310

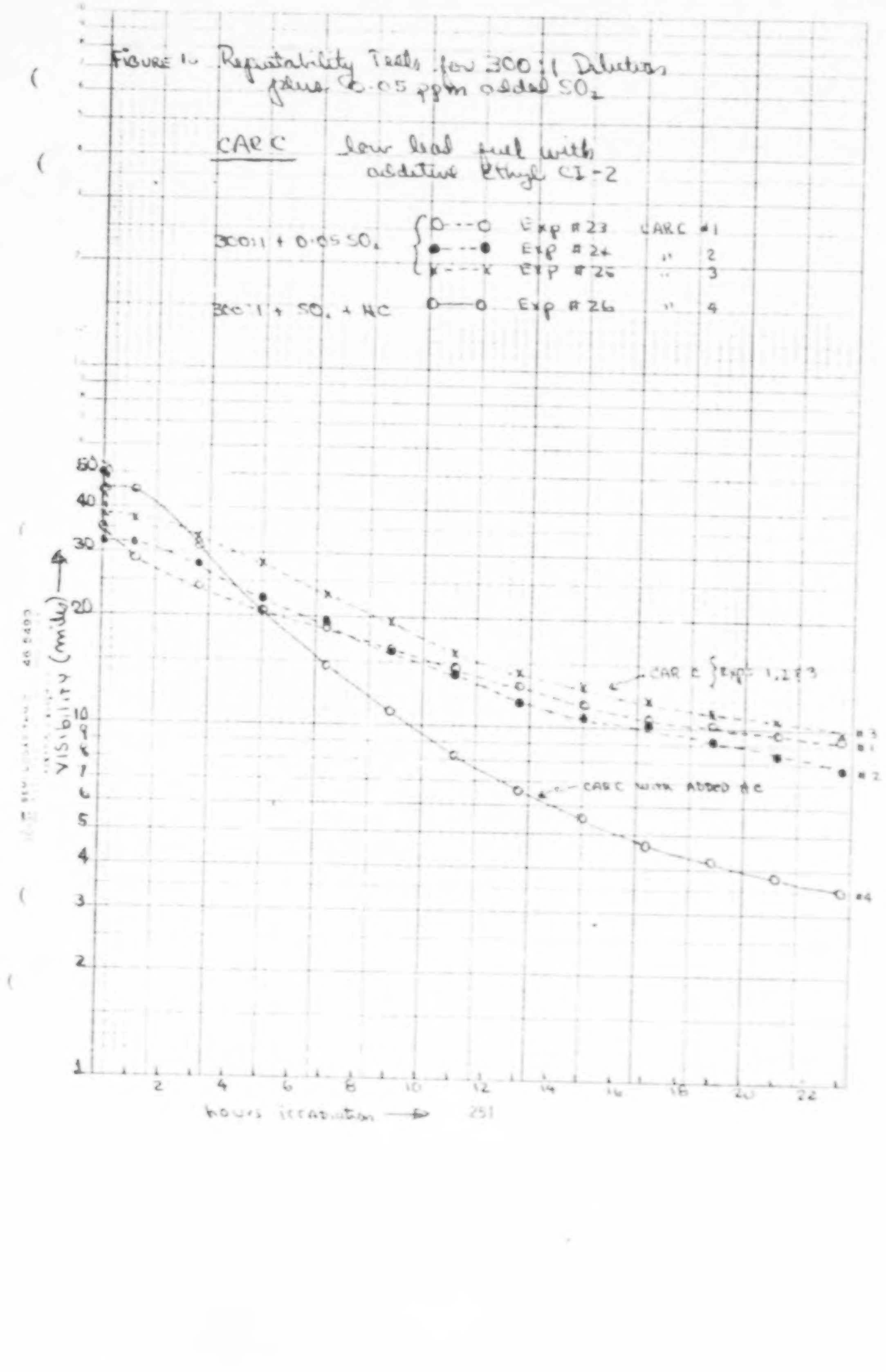


FIGURE 16 Repeatability Tests for 300:1 Dilutions plus 0.05 ppm added SO_2

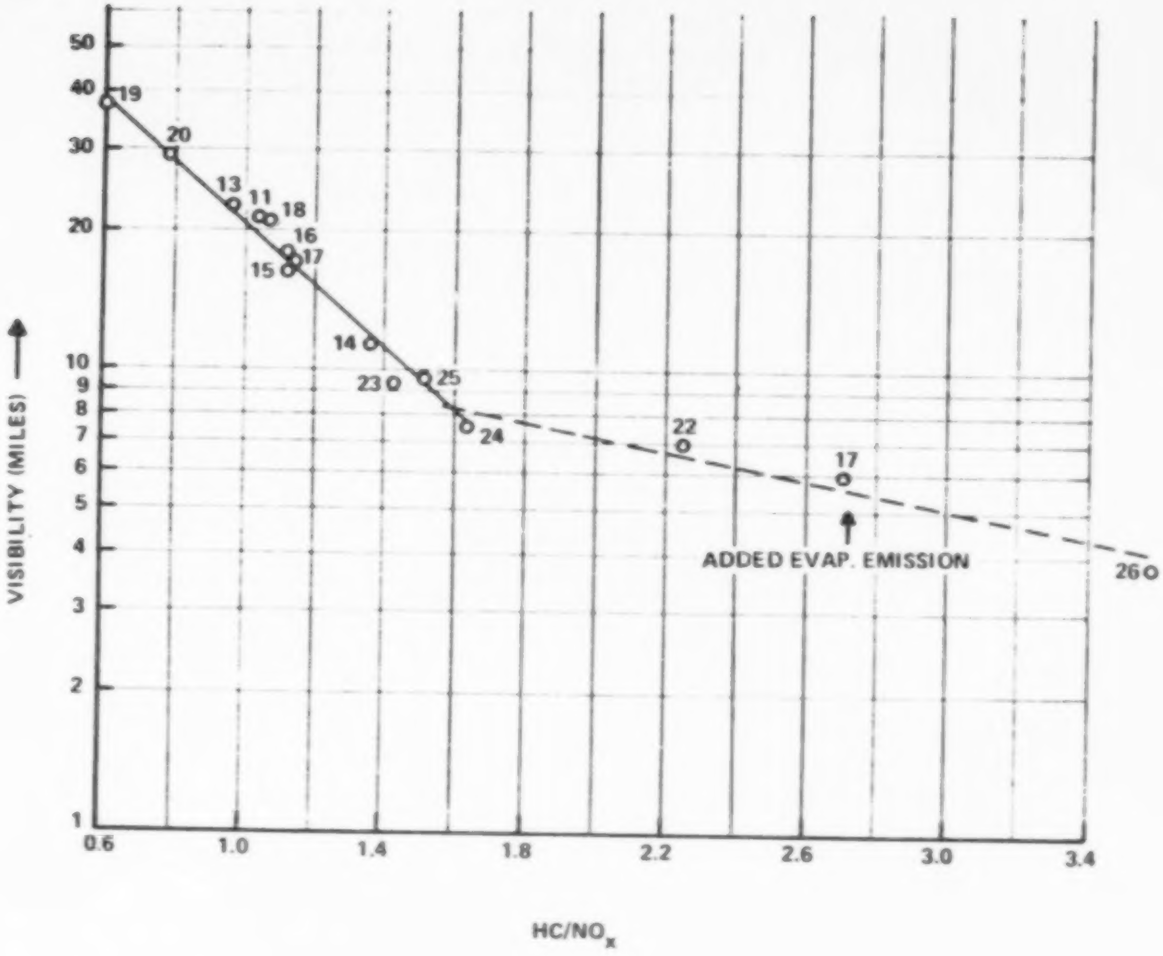


Figure 17 FINAL VISIBILITY IN SMOG CHAMBER VS HC/NO$_i$ RATIO (TEST NUMBER SHOWN ADJACENT TO EACH DATA POINT)

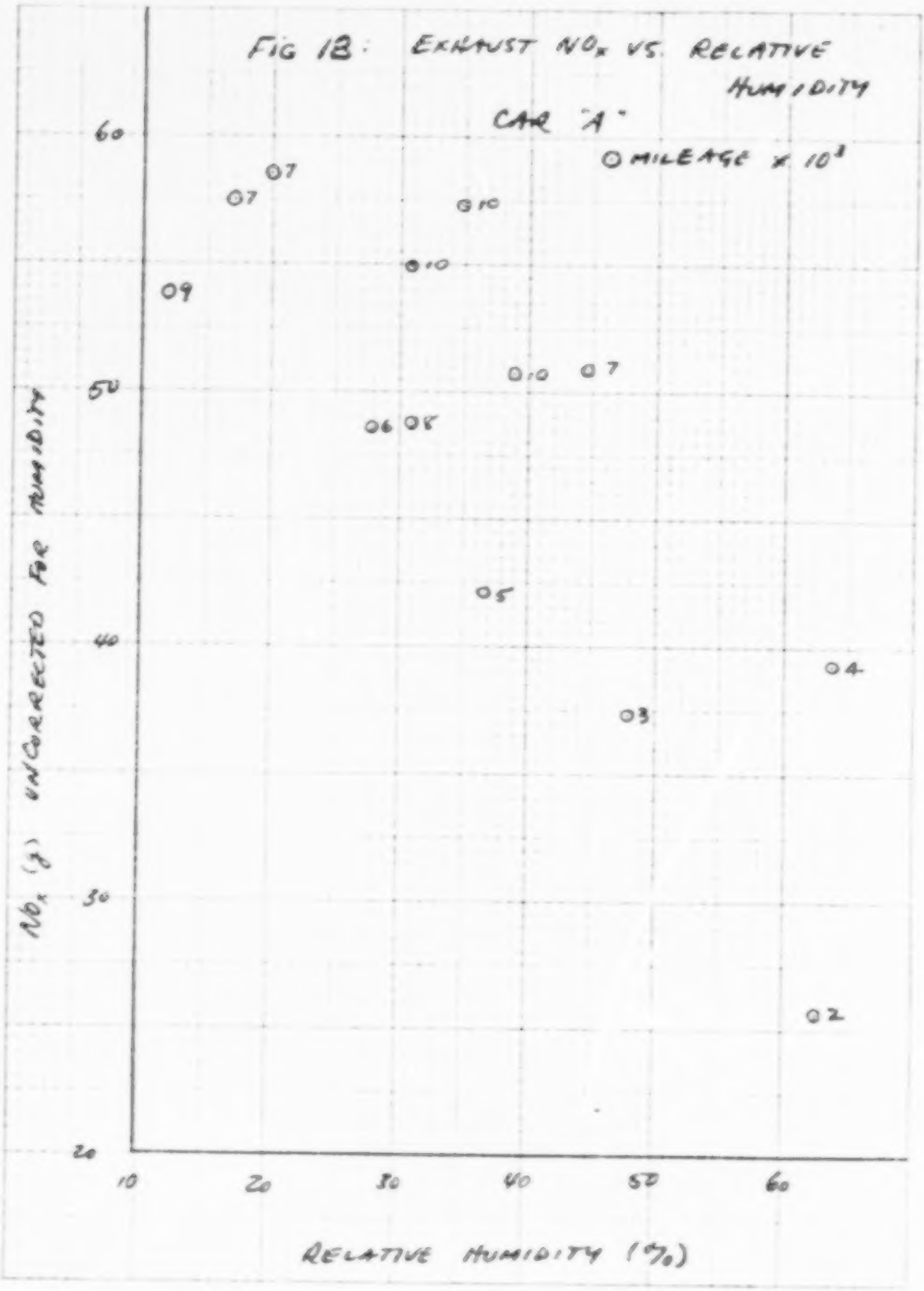
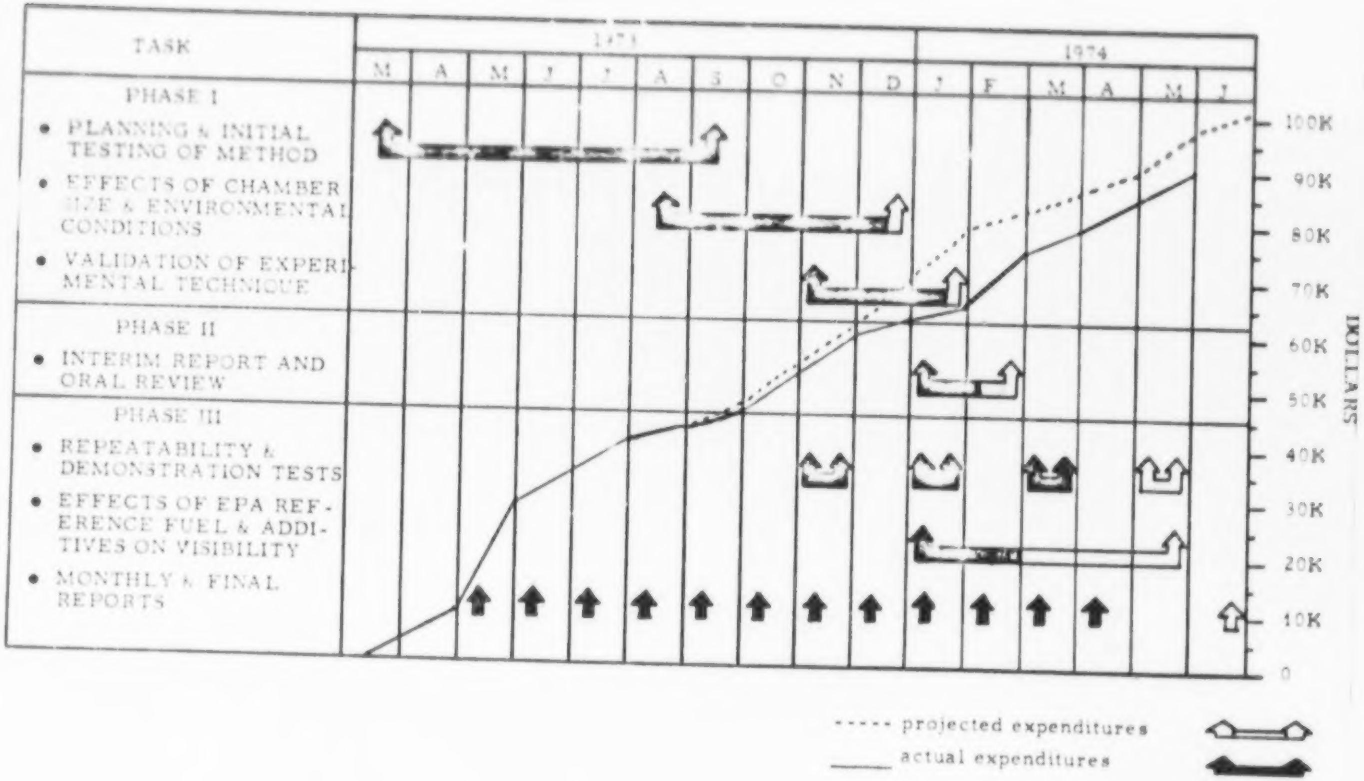


FIG 1B: EXHAUST NO_x VS. RELATIVE HUMIDITY

CAR "A"

Figure 17 PROGRAM SCHEDULE AND CUMULATIVE COSTS - REVISED 9/10/73



APPENDIX B7.1B

DEVELOPMENT OF A METHODOLOGY TO DETERMINE THE EFFECTS OF FUEL AND ADDITIVES ON ATMOSPHERIC VISIBILITY

MONTHLY LETTER REPORT
FOR PERIOD COVERING SEPTEMBER 1974

By: W. C. Kocmond

Contract No. 68-02-0698

10 October 1974

Prepared for:

Environmental Protection Agency
Durham, North Carolina

- ## INTRODUCTION

One of the provisions of the 1970 amendment to the Clean Air Act stipulates that the Administrator of the Environmental Protection Agency (EPA) may require a fuel or fuel additive manufacturer to conduct specific tests in accordance with accepted test methods and procedures to determine the effect of such emissions on the public welfare or on the emission control performance of a vehicle. The contribution of these emissions to reduced visibility in the atmosphere is related to this problem and therefore must also be considered. In order to anticipate possible regulatory measures, a methodology is required for assessing the effects of fuels and/or fuel additive combustion products on atmospheric visibility. It is the objective of this investigation to develop such a methodology.

In this monthly report, a brief description is given of progress for the month of September, together with plans for the coming month.

- ## PROGRESS TO DATE

During September and early October, engine tear down procedures were completed on Cars A and B and mileage accumulation was started. New exhaust systems were installed on both vehicles and all combustion chamber deposits were collected for EPA inspection and analysis. A decision to replace the heads from Car A with those from C (no longer slated for tests on this programs) was made after noting that the valve guides in Car A were wearing abnormally. This condition could have posed a threat to proper engine operation after additional mileage accumulation.

A 1973 Ford Torino with a catalytic converter was delivered to Calspan from the EPA during late September. The car is being operated on lead-free reference fuel in the same manner as A and B during the mileage accumulation period. All vehicles will be given an emissions test after the 1000 mile point is reached.

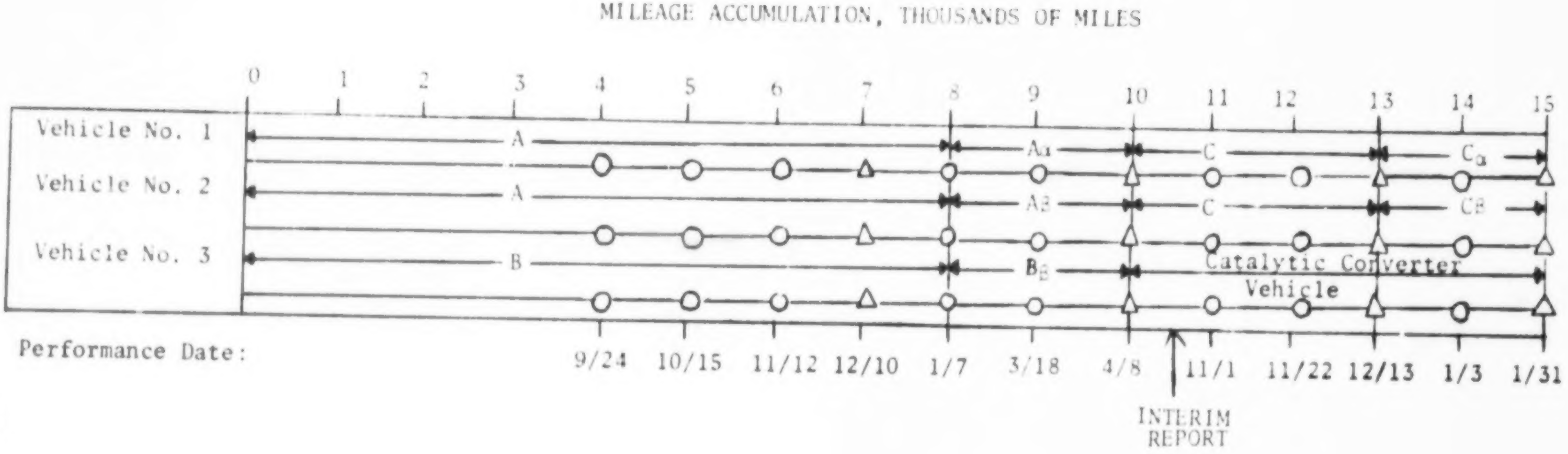
Work was completed during September on the air conditioning system which will be used to supply controlled humidity air to the carburetors of the vehicles during emissions tests. The system, which consists of a 1 ton air conditioner, reheat coils, blowers and appropriate ductwork, has been tested over a wide range of humidities and temperatures and is operating satisfactorily. Humidities between 30% and 80% can be reliably obtained by regulating the amount of heat that is supplied to the nearly saturated cold air within the ductwork. The system will be used during the first emissions series scheduled for late October.

• PLANS FOR THE COMING MONTH

Mileage accumulation will continue during October and the first emission series will be performed on the test vehicles late in the month. A total of 3000 miles will be driven on Cars A and B before additives are introduced into the fuels. The catalytic converter equipped Ford will operate on reference fuel throughout the period.

Because of delays in completing the lighting modifications to the Calspan smog chamber, methodology tests will not be started until early November. The vehicle emission test schedule anticipated for the remainder of the program is shown in Figure 1.

FIGURE 1. REVISED VEHICLE EMISSION TEST SCHEDULE



LEGEND

1. ○ = MILEAGE CONDITIONING TEST (SINGLE TEST)
2. △ = REPRODUCIBILITY DEMONSTRATION TESTS (TRIPLICATE TESTS)
3. A = INDOLENE 0
   B = INDOLENE 0 + 0.5 GM/GAL TEL
   C = EPA REFERENCE FUEL
4. α = CHEVRON F-310
   β = ETHYL CI-2

NOTES:

1. AN UNSPECIFIED NUMBER OF PRELIMINARY TESTS WILL BE PERFORMED DURING THE FIRST SEVEN THOUSAND MILES
2. EACH ENGINE WILL BE CLEANED AND A NEW EXHAUST SYSTEM INSTALLED AFTER THE FIRST TEN THOUSAND MILES.

APPENDIX B7.2

DEVELOP LABORATORY METHOD FOR THE COLLECTION AND ANALYSIS OF SULFURIC ACID AND SULFATES (21 BCE - 053)

The primary source of atmospheric sulfuric acid aerosols and sulfates is the burning of fossil fuels that contain sulfur compounds. Photochemical and catalytic reactions in the atmosphere produce additional quantities of sulfuric acid and sulfate. The United States will be emitting much more sulfuric acid and sulfate into the atmosphere as a result of the catalytic converter that must be installed on all 1975 vehicles. In addition, the burning of more coal with a high sulfur content will compound the sulfuric acid-sulfate problem. The toxicity of sulfuric acid aerosols and their ever-increasing input to the atmosphere makes it imperative that a reliable, specific, and sensitive sulfuric acid and sulfate method be developed.

A contract is being written entitled "Development of Methodology and Instrumentation for the Assay of Sulfuric Acid and Sulfates in Ambient Air." It should be in the Contracts Office by the end of August 1974 and hopefully proposals will be received for evaluation and contractor selection by November 1974.

APPENDIX B7.3

DEVELOP PORTABLE DEVICE FOR COLLECTION OF SULFATE AND SULFURIC ACID (21 BCE - 052)

Sulfuric acid and sulfate present in the atmosphere constitute severe health hazards. The emission and consequently the adverse effect on human health of increasing amounts of these pollutants caused by the increasing use of catalytic converters on automobiles can properly and reliably be assessed only if accurate and reliable collection methods exist. Presently available samplers and sampling techniques for sulfuric acid and sulfate are unsatisfactory, mainly because no provisions have been made to check or prevent the conversion of SO_2 to sulfuric acid and/or sulfate on the collection medium nor to prevent interactions of hydrocarbons, photochemical oxidants, and a host of airborne catalytic substances with the sulfur oxides.

The purpose of this task, therefore, is to evaluate present sampling methods and to develop a compact, efficient, and economic portable collection device for sulfuric acid and sulfate whereby artifact formation is prevented and precursors of sulfuric acid and sulfate are not collected as sulfuric acid or sulfate so that the values of $\mu g/m^3$ of these two pollutant species are accurate values representing the true amounts of sulfuric acid and sulfate at the site of collection.

Task 052 is presently in the planning stage and no RFP has yet been issued. It appears that the target date for completion of the task (July 1975) as listed in ROAP 21 BCE is premature and unrealistic, and it is suggested that it be rescheduled.

APPENDIX B7.4

PERSONAL EXPOSURE METERS FOR SUSPENDED SULFATES

(21 BCE - 041)

This program will include development of devices to collect particles so that analysis for H_2SO_4 may be performed shortly after the sample is deposited on the collection surface. This collection device after initial testing could be converted to a miniature personnel dosimeter, if we can demonstrate that the sulfuric acid collected will maintain its integrity until the collector is returned to the laboratory for analysis.

APPENDIX B7.5

Smog Chamber Study of SO_2 Photo-oxidation to SO_4 Under Roadway Conditions

This is a contract task performed by Calspan Corporation. The task calls for smog chamber experimentation to determine the dependence of sulfate formation on the sulfate precursors, in simulated roadway atmospheres. This work is coordinated with another contract effort at Battelle, concerned with sulfate formation in city-wide and rural atmospheres. Detailed design and coordination of the two efforts was finalized in an EPA-Calspan-Battelle meeting held in RTP, NC in June, 1974. Calspan is now completing a first phase of the study, concerned with delineation of effects from certain chamber design and procedural factors upon the data sought. Information to be ultimately generated in this project will provide a measure of the extent to which SO_2 is expected to be converted into sulfate in a typical roadway atmosphere.

APPENDIX B7.6

STUDY OF SCAVENGING OF SO_2 AND SULFATES BY SURFACES NEAR ROADWAYS (PE 1AA002, ROAP A21BCE Task 049)

This is a new task that will be performed under contract. An RFP should be out in September and the contract awarded in December.

Existing diffusion models do not include pollutant removal mechanisms at surfaces although empirically determined distribution parameters (σ_z, σ_y) very likely account for this effect. Roadway and adjacent surfaces may act as significant sinks for auto produced SO_2 (controlled by eddy diffusivity) while not acting in the same way for fine ($<.1\mu$) aerosol H_2SO_4 (controlled by Brownian movement through boundary layer). These effects should be determined and incorperated into diffusion models.

The contract will call for four related research efforts. These efforts are (1) theoretical diffusion modeling to estimate the relative effects of surfaces as sinks for reactive gases and aerosols, (2) laboratory controlled experiments to determine magnitude of these effects on various surfaces for SO_2 and H_2SO_4 aerosols, (3) field controlled experiment (measuring concentrations from controlled emissions over uniform surface such as unused airport runway), and (4) correlating deposition rates on various surfaces with concentration, emission, and meteorological data near high traffic density roadways to verify controlled experiment findings.

APPENDIX B7.7

Characterization of Roadside Aerosols

St. Louis Roadway Sulfate Study

Grant, Husar, Washington University, St. Louis, Missouri

The objective of this study is to determine the changes in sulfate aerosol, sulfuric acid mist, and other aerosols components due to the introduction of cars equipped with catalysts. This will differ from the Los Angeles study in that it will be performed in a city with higher SO_2 background, lower oxidant, and different meterological conditions. Sulfate size distribution, SO_2/ sulfate ratio, 2-hour sulfate and other elements, and acidity will be measured upwind and downwind of a beltway with approximately 250,000 vehicles a day traffic.

The elemental analysis will be performed by Winchester, Florida State University, Tallahasse. Husar, at Washington University, will make water soluble sulfate and acidity measurements for both roadway studies.

This program will be coordinated with other studies in St. Louis which are part of the RAPS program. It is expected that meteorological and vehicle emission data will be available from RAPS.

21BCE-40 SRO 61ABZ Atmospheric Chemistry of Acid Aerosols

ROAP 21AKB, Determination of the Character and Origin of Aerosols, contains a number of programs relevant to the problem of acid aerosols. The ROAP output is described as follows:

> Contribution of the major sources to atmospheric aerosols, quantitative descriptions of the generation and removal rates associated with each major source and sink, characterization of urban, natural, primary source and secondary source aerosols, scientific data for fine particle criteria and standards, quantification of the effects of aerosols on atmospheric chemical reactions.

> The ROAP approach is described as follows:

> Determine physical and chemical properties of source, ambient, and natural aerosols; use this information to infer the contribution of the various source to the ambient atmospheric aerosol loading; determine generation and removal rates for important sinks and sources; measure effects of various aerosols on atmospheric chemical reactions; study gas-particle conversions and particle removal processes. Establish the relation between photochemical aerosol concentrations and concentrations of controllable precursors. Special attention will be given to sulfates, nitrates, Cd and Pb.

This ROAP contains a number of programs which are of special interest to the Catalyst Program.

1. Photochemical Generation of Acid Aerosols from SO_2. Smog chamber studies are being conducted to resolve current problems over the rate of the direct photochemical generation of sulfuric acid mist from SO_2. Reported rates vary from a low of no reaction reported by Friend to a rate of 6% per hour obtained in the Battelle Smog Chamber. Studies will be conducted to determine the reasons for the variation in reaction rates and to determine the mechanism of this reaction.

2. Indirect photochemical or chemical conversion of SO_2 to sulfuric acid mist. Laboratory studies have been conducted on the olefin, ozone, SO_2 system which indicate that sulfuric acid mist is formed by the oxidation of SO_2 by a biradical or zwitterion, a reactive species formed from the reaction of ozone plus olefin. A mechanism has been derived for this process and rates recommended for the photochemical model of sulfate formation from this system. Further work will be performed to obtain more accurate rates and mechanisms. Additional studies will be made to determine rates and mechanisms for other conversion mechanisms. Smog chamber studies are being conducted of the olefin, NO_x, SO_2 system. Studies this year will be with propylene. The data from the smog chamber studies will be used to improve and validate the photochemical smog model.

3. Liquid dropplet reactions. Studies are being conducted to determine the rates and mechanisms and effects of catalyst such as

metal salts and ammonium on the conversion of SO_2 to sulfate in liquid dropplets or liquid aerosols of various types. It is felt that this heterogenous mechanism may be very important both in power plant plumes and in the conversion of SO_2 to sulfate during long range transport. It may also be important near roadways under conditions in which fog is formed.

4. Surface reactions. Studies are being conducted to determine the chemical structure of SO_2 absorbed on atmospheric particles and to measure the rate of conversion of SO_2 to sulfate on a variety of atmospheric particles and surfaces.

5. Size distribution measurement. Both impactors and particles counting techniques are being used to determine the size distribution of aerosol generated by automobiles and other sources and at various points in the atmosphere.

6. Aerosol Dynamics. Theoretical and experimental studies are being conducted on the nucleation of sulfuric acid mist and the condensation and coagulational growth of sulfuric acid particles.

7. Humidity effects. The size of the sulfuric acid aerosol depends strongly on the relative humidity. Sulfuric acid particles will grow if the relative humidity increases above about 20%. An experimental appartus is being constructed to allow measurements of the aerosol growth and theoretical calculations are being develcped to calculate the aerosol growth under conditions of relative humidity from 20-100%. This may be specially important in determining lung deposition. Sulfuric acid mist from automobiles is thought to be in the fine particle range with estimates from .02 to .3 for the mass

mean diameter. These particles will probably be carried into the lung during breathing. If they were inert a large percentage of them would be expected to escape from the lung. However, the sulfuric acid dropplets will grow in the high humidity of the respiratory system and will be deposited on the lung or bronchi tissue by impaction.

8. Sulfate compounds. An insitu technique has been developed and used in the field which provides qualitative differentiation between sulfuric acid droplets, ammonium bi-sulfate, NH_4HSO_4, and ammonium sulfate,, $(NH_4)_2SO_4$.

9. Aerosol generation. Techniques have been developed for generating sulfuric acid mist in the .1 to .3 micron size range for use in animal exposure studies.

10. Sulfate analysis. Techniques have been developed using flash vaporization and flame photometric detection to measure either total sulfur compounds volatile at 800°C or total water soluble sulfur compounds. This technique is sensitive down to a few nanograms of sulfur and can be used to make very short time measurements of sulfur containing aerosols.

APPENDIX B7.8

CHARACTERIZATION OF ROADSIDE AEROSOLS

Los Angeles Roadway Sulfate Study
Grant: Winchester, Florida State University
Tallahassee, Florida

The primary objective of the first phase of this study is to obtain pre-catalyst, baseline information on aerosol characteristics to permit assessment of changes caused by catalyst equiped automobiles. Of special interest is the sulfate/SO_2 ratio, the size distribution of the sulfate aerosol, and the acidity of the aerosol. The baseline data will be obtained by monitoring the ambient air adjacent to a heavily traveled highway before the 1975 model year, catalyst equipped automobiles are on the road. A series of tests will be conducted along a Los Angeles, California, freeway early in September, 1974, to provide some of the baseline information. Analyses for elements, sulfate, acidity and size distribution will be correlated with SO_2 and CO concentrations and meteorological data obtained in the QAEML study. Later in the fiscal year, after catalyst equipped cars are present in the automobile mix, the study will be repeated to determine the changes caused by catalyst cars.

Aerosol particles will be collected as a function of particle size, using cascade impactors of the single orifice Battelle design, and of time, using Jensen-Nelson "streaker" Nuclepore filter samplers. Six impactor fractions from <0.25 to >4 μm diameter will be collected over 8-16 hour sampling intervals, and unfractionated aerosol will be sampled by "streaker" with 2 hour time resolution. Some samplers will be activated by a wind direction sensitive switching device. Samplers will be taken at established stations operated by the EPA in Los Angeles along a freeway where SO_2, CO, and wind velocity are monitored during aerosol sampling. For periods of optimum meteorological conditions, aerosol samples will be selected for elemental analysis using proton-induced x-ray emission (PIXE) with the view of relating observed atmospheric concentrations to sources along the freeway and in directions toward and away from the ocean. These results may provide a baseline for future measurements to evaluate the freeway as a source, especially of particulate sulfur compounds. Duplicate impactor and streaker samples will be taken for determination of water soluble sulfate by flash vaporization followed by flame photometric. Low pressure impactor runs will be made to determine the size distribution in the range 0.05 to 1.0 microns.

We can expect to find the following results:

The PIXE analytical technique permits quantitative measurement of S, Cl, K, Ca, Ti, Fe, Zn, Br, and Pb in most aerosol samples of 1 m^3 air volume from urban areas, and V, Cr, Mn, Ni, Cu, and As may be determined as well. The present work will focus on sulfur and the elements which can be related to it. Relations of the following kind will be looked for in the data from this baseline study:

If future particulate sulfur is derived from auto exhausts, assuming it is formed during the combustion of unleaded gasoline, its secular increase should be correlated with a secular decrease in atmospheric lead. There, the present extent of correlation of particulate sulfur with lead, especially as a function of particle size, may be a crucial part of the baseline information in this study.

Future acid sulfate additions along the freeway may cause chemical reactions in the ambient aerosol, especially if sufficient time is available for particle interactions in the atmosphere. Volatility of Cl and Br by acidification is one type of reaction which may occur. Therefore, future sulfur increases may be accompanied by decreases in Cl and Br concentrations and in the relative Br/Pb of automotive exhaust particles. Present correlations between these elements should be part of the baseline.

The ambient aerosol is affected by natural sources at sea, which generate large amounts of large particle chloride, and sulfate, and on land, which generate large particles of soil composition, including Fe and Ti, and additional urban sources may also be operative, affecting the concentrations of Pb, Br, S, and other elements, especially in small particle size ranges. The baseline study, through statistical treatment of the data, will examine the relationships among all the elements measured so that the net freeway contributions to the aerosol may be evaluated. Future studies will be compared with these general baseline relationships.

Samples of fine and coarse aerosol will also be collected for determination of total acidity. This will give an indication of the amount of acid currently present in roadway aerosol. Analysis of samples for acidity and water soluble sulfate willbbe performed at Washington University, St. Louis. This program will include PIXE analysis of samples collected in St. Louis for the St. Louis Roadway Sulfate Study.